DIE ZWEIDIMENSIONALE ZUSTANDSGLEICHUNG UND DER BAU VON GRENZFLÄCHENSCHICHTEN.*

Von Bunichi TAMAMUSHI.

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Teil II. Die Oberflächenschicht reiner Flüssigkeiten.

1. Die Zustandsgleichung der Oberflächenschicht reiner Flüssigkeiten.

Die Ansicht, dass an der Oberfläche dielektrischer Flüssigkeit eine durch die Molekularkräfte hervorgebrachte Orientierung von Molekülen bestehe, ist besonders von Lenard,[37] Langmuir[38] und Harkins[39] vertreten worden. Die Langmuir-Harkinssche Vorstellung, dass sich solche Flüssigkeitsmoleküle, die sowohl nonpolare wie polare Gruppen enthalten, z. B. Fettsäuren an der Oberfläche derart richten, dass die nonpolare Gruppe ($-CH_3$) an der Oberfläche nach aussen gerichtet, die stark polare Gruppe (-COOH) nach dem Flüssigkeitsinnern gerichtet steht. Tatsächlich konnte man, in Übereinstimmung mit dieser Vorstellung, zeigen, dass die Oberflächenspannung bzw. die gesamte Oberflächenenergie der homologen organischen Flüssigkeiten (Alkohole, Fettsäuren) unabhängig von der Molekulargrösse gleichwertig ist;[40] die Oberfläche der homologen Flüssigkeiten verhalten sich deshalb als ob sie nur durch die inaktive Gruppe ($-CH_3$) gebildet wäre. Es wird also wohl erwartet, dass die Moleküle auch an der Oberfläche reiner Flüssigkeiten, ganz analog der adsorbierten Schicht auf Wasser, stabartig stehen und zwar bei der kurzen Reichwerte der Molekularkräfte wird eine derartig orientierte Schicht sich an der Oberfläche monomolekular bilden,[41] wenn auch die thermische Bewegung der Moleküle dagegen stets störend wirkt. Es scheint dann berechtigt, auch für die Oberfläche reiner Flüssigkeiten analog der adsorbierten Schicht eine zweidimensionale Zustandsgleichung aufzustellen, die im folgenden formuliert wird.

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* Die Fortsetzung aus S. 393 dieses Bandes.

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(37) Lenard, *Sitzungsber. d. Heidelberger Akad. d. Wiss. Math. Natw. Kl.*, 1914, 27, 28, 29.

(38) Langmuir, *J. Am. Chem., Soc.*, **38** (1916), 2231; **39** (1917), 1848.

(39) Harkins u. Mitarbeitern, *J. Am. Chem. Soc.*, **39** (1917), 354; 541; **42** (1920), 700; **43** (1921), 35; **44** (1922), 653.

(40) Hunten u. Maas, *J. Am. Chem. Soc.*, **51** (1929), 153.

(41) Vgl. Einstein, *Ann. Physik*, (4), **34** (1911), 165.

Man nimmt an, dass das Flüssigkeitsmolekül eigentlich an der Oberfläche die laterale freie Beweglichkeit besitzt, die aber durch die auf das Molekül gleichzeitig wirkenden starken Kohäsionskräfte weitgehend gehindert wird. Durch die Differenz dieser zwei Effekte wird dann der messbare äussere Oberflächendruck angegeben. Man denkt sich nun auf der Oberfläche zwei Flächenteilchen, die sich jedes für sich in der Temperatur T und $T+\Delta T$ befinden und mit einer geschlossenen Linie voneinander begrenzt sind. In Wirklichkeit können solche Flächenteile von verschiedener Temperatur offenbar nicht im Gleichgewicht sein, aber es wäre doch gestattet, dies begrifflich anzunehmen. Nun hat der Flächenteil $T+\Delta T$ die Oberflächenspannung σ und der Flächenteil T die Oberflächenspannung $\sigma+\Delta\sigma$ und somit wirkt die nach dem Flächenteil T hinziehende Kraft $d\sigma$ auf das Linienelement der Grenze, infolgedessen versucht sich der Teil $T+\Delta T$ nach aussen auszudehnen. Bezeichnet man diese Ausdehnungskraft (pro Linienelement) mit $d\Pi$, so wird:

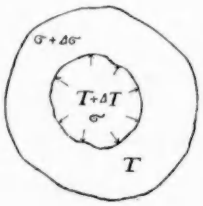


Fig. 6.

$$d\Pi = -d\sigma\,.$$

Integriert dies von der tiefsten Temperatur T_0 bis zur Messungstemperatur T, so ergibt sich:

$$\Pi = \int_{T_0}^{T} d\Pi = -\int_{T_0}^{T} d\sigma = \sigma_0 - \sigma\,, \qquad (1)$$

wo σ_0 die Oberflächenspannung in T_0, und σ die Oberflächenspannung in T bedeutet. Angenommen ist hier, dass T_0 eine solche Temperatur ist, bei der keine thermische Bewegung mehr stattfindet, so würde σ_0 einen rein statischen Anteil der Oberflächenspannung darstellen. Der wirkliche Wert von σ_0 ist aber keineswegs zu ermitteln bei unseren gegenwärtigen unzulänglichen Kenntnisse über die Natur der Molekularkräfte. Ich nenne hier σ_0 die statische Oberflächenspannung.

Nun bedeutet Π den Oberflächendruck, mit dessen Hilfe wird die Zustandsgleichung der Flüssigkeitsoberfläche analog der adsorbierten Schicht mittels der Virial-Methode abgeleitet. Nimmt man auch hierbei zwischen den Molekülen eine Kraft in der Form $-\frac{\partial E}{\partial r}$ an, so wird die allgemeine Zustandsgleichung für ein Molekül: (Vgl. I. 4.)

$$\Pi\omega = \frac{1}{2} m v^2 - \frac{1}{2} r \frac{\partial E}{\partial r}\,, \qquad (2)$$

wobei ω die Fläche eines Moleküls bedeutet. Verwendet man hierfür den Energie-Gleichverteilungssatz, so bekommt man:

$$\Pi\omega = kT - \frac{1}{2} r \frac{\partial E}{\partial r},$$

wo k die Boltzmannsche Konstante ist. Summiert man diese Gleichung über alle Paare der Moleküle in der Molaroberfläche der Flüssigkeit, unter Berücksichtigung:

$$\Omega = (Nv)^{\frac{2}{3}} \quad \text{und} \quad v^{\frac{2}{3}} = \omega,$$

wo N die Loschmidtsche Zahl und v das Volum eines Moleküls (kinetisch als Kugel betrachtet) bedeutet, so ergibt sich: (Vgl. I. 5.)

$$\Pi\Omega = N^{\frac{2}{3}} kT - \frac{1}{2} \frac{N^{\frac{4}{3}}\pi}{\Omega} \int_0^\infty r^2 \frac{\partial E}{\partial r} e^{-\frac{E}{kT}} dr.$$

Durch Integration folgt:

$$\Pi\Omega = N^{\frac{2}{3}} kT - \frac{N^{\frac{4}{3}}\pi}{\Omega} kT \int_0^\infty r(e^{-\frac{E}{kT}} - 1) dr, \qquad (3)$$

oder

$$\Pi\Omega = N^{\frac{2}{3}} kT \left(1 + \frac{B}{\Omega}\right); \qquad (4)$$

wobei für den zweiten Virialkoeffizient B eingesetzt ist:

$$B = N^{\frac{2}{3}}\pi \int_0^\infty r(1 - e^{-\frac{E}{kT}}) dr.$$

Diese Gleichung (4) ist die Zustandsgleichung der Oberflächenschicht reiner Flüssigkeiten, die im folgenden noch näher erläutert werden soll.

2. Theorie der Temperaturabhängigkeit der Oberflächenspannung.

Die Zustandsgleichung (4):

$$\Pi\Omega = N^{\frac{2}{3}} kT + N^{\frac{2}{3}} kT \cdot \frac{B}{\Omega}$$

wird zweckmässigkeitshalber auch in die folgende Form gefasst:

$$\Pi\Omega = N^{\frac{2}{3}} kT - \Phi(r), \qquad (5)$$

wo $\Phi(r)$ die Wechselwirkungsenergie (pro Molaroberfläche) zwischen den Molekülen darstellt. $\Phi(r)$ ist im allgemeinen temperaturabhängig. Diese Beziehung ähnelt der Grundannahme in der van der Waals-Hulshofschen Theorie der Kapillarität,[42] indem sie besagt, dass der äussere manometrische Druck der Differenz zwischen thermischem und innerem Kohäsionsdruck gleich ist. Aber die hier angegebene Betrachtung unterscheidet sich im prinzipiellen von der van der Waals-Hulshofschen Theorie darin, dass sie in der Kapillarschicht nicht stetigen Dichtabfall sondern plötzlichen Dichtabfall annimmt. Die Gleichung (5) lässt sich schreiben:

$$(\sigma_0-\sigma)\Omega = N^{\frac{2}{3}}kT-\Phi(r)\,,$$

oder

$$\sigma\Omega = \sigma_0\Omega-N^{\frac{2}{3}}kT+\Phi(r)\,. \qquad (6)$$

Dies auf die Flächeneinheit gerechnet:

$$\sigma = \sigma_0- n^{\frac{2}{3}}kT+\varphi(r)\,, \qquad (7)$$

wo $n^{\frac{2}{3}}$ die Molekülzahl in der Flächeneinheit, $\varphi(r)$ die Wechselwirkungsenergie pro Flächeneinheit bedeutet. Diese letzte Beziehung gibt eine Definition der Oberflächenspannung, nämlich: die Oberflächenspannung (Erg/qcm) ist gleich der Differenz der zwischenmolekularen und thermischen Energie, wobei die zwischenmolekulare Energie aus zwei Teilen besteht, ein rein statischer (σ_0) einerseits und ein temperaturabhängiger ($\varphi(r)$) anderseits.[43]

Die Beziehung (6) bzw. (7) drückt gleichzeitig das Gesetz der Temperaturabhängigkeit der Oberflächenspannung aus, es enthält also die Eötvössche Formel als eine speziale Folgerung. Für die kritische Temperatur (ϑ_0) der Flüssigkeit, wird σ gleich null und so folgt aus Gleichung (6):

(42) van der Waals-Kohnstamm, „Lehrbuch d. Thermodynamik," I, (1927), S. 318.

(43) Diese Beziehung lässt sich mit den Born-Courantschen sowie Brillouinschen Beziehungen vergleichen. Nach Born und Courant (*Physik. Z.*, **14** (1913), 731) gilt:

$$\sigma = \sigma_0-2\pi\left(\frac{kT}{hc}\right)^2 kT\int_0^{x_m}\frac{x^2}{e^x-1}dx\,,$$

und nach Brillouin (*Comp. rend.*, **180** (1925), 1248.)

$$\sigma = \sigma_0-\frac{9}{4}\frac{NkT}{S_m}\,,$$

wo, in den beiden Beziehungen, σ_0 den statischen Bestandteil der Oberflächenspannung und das zweite Glied in der rechten Seite eine Funktion der Temperatur darstellt.

$$\sigma_0 = \frac{N^{\frac{2}{3}} k \vartheta_0}{\Omega} ,$$

unter der Bedingung, dass auch der Virialkoeffizient B bzw. $\Phi(r)$ für die kritische Temperatur gleich null gesetzt werden kann. Dies in Gleichung (6) eingesetzt, so ergibt sich:

$$\sigma\Omega = N^{\frac{2}{3}} k(\vartheta_0 - T) + \Phi(r) , \tag{8}$$

oder

$$\sigma\Omega = N^{\frac{2}{3}} k\left\{1 + \frac{\Phi(r)}{N^{\frac{2}{3}} k(\vartheta_0 - T)}\right\}(\vartheta_0 - T) . \tag{9}$$

Setzt man weiter:

$$N^{\frac{2}{3}} k\left\{1 + \frac{\Phi(r)}{N^{\frac{2}{3}} k(\vartheta_0 - T)}\right\} = K \tag{10}$$

ein, so wird:

$$\sigma\Omega = K(\vartheta_0 - T) ,$$

was die Eötvössche Formel wiedergibt, wo K aber nicht mehr eine einfache Konstante, sondern eine Funktion ist, die im allgemeinen von Stoff zu Stoff verschieden und auch von der Temperatur abhängig sein soll.

Bevor ich auf die Analyse dieser Gleichungen eingehe, möchte ich hier einiges über die Geschichte des Eötvösschen Gesetzes berichten. Das Gesetz, das meist in die Form:

$$\sigma V^{\frac{2}{3}} = K(\vartheta_0 - T) \tag{11}$$

gefasst wird, wurde zuerst von Eötvös[44] rein empirisch aufgestellt, wo V das Molarvolum und K eine Konstante bedeutet, die weitgehend von der Flüssigkeit unabhängig war. Diese Formel wurde dann von Ramsay und Shields[45] eingehend geprüft, sie gaben eher der empirischen Beziehung die folgende Form:

$$\sigma V^{\frac{2}{3}} = K'(\vartheta_0 - T - \tau) , \tag{12}$$

wo K' eine Konstante ist; τ ist der kleine Betrag (6°) den man von der kritischen Temperatur abziehen muss, um den Schnittpunkt der σ, T-Geraden mit der T-Achse zu erhalten. Katayama[46] vermied diese willkürliche Konstante und stellte die Formel:

(44) Eötvös, *Wied. Ann.*, **27** (1886), 448.
(45) Ramsay u. Shields, *Z. physik. Chem.*, **12** (1893), 433.
(46) Katayama, *Science Rep. Tohoku Imp. Univ.*, **4** (1915), 373.

$$\sigma\left(\frac{M}{\rho_f-\rho_g}\right)^{\frac{2}{3}} = K''(\vartheta_0-T) \qquad (13)$$

auf, wo M das Molargewicht, ρ_f die Dichte der Flüssigkeit, ρ_g die Dichte des Dampfes, der mit der Flüssigkeit im Gleichgewicht steht und K'' eine Konstante bedeutet. Diese Formel hat die Vorzüge, dass sie nicht nur die empirischen Daten über einen grösseren Bereich der Temperatur wiedergibt, sondern auch, dass sie mit der Theorie der übereinstimmenden Zustände im Einklang steht.

Die Konstante K bzw. K', K'', in Gleichungen (11) bzw. (12), (13) erwies sich für eine Anzahl der Flüssigkeiten mit mittlerem Molargewicht, die man gewöhnlich als normal betrachtet, als konstant und zwar gleich dem Wert von rund 2. Aber nach den umfangreichen Untersuchungen von Walden,[47] Morgan,[48] Jaeger[49] und andern erwies sich sie keineswegs einfach als konstant. Eine Klasse von Substanzen, zu der z. B. Äthylalkohol, Essigsäure, Wasserstoff, Helium, geschmolzene Metalle und Salze gehören, hat kleineren Wert als 2, und eine andere Klasse, zu der meist hochmolekulare Verbindungen wie höhere Fettsäuren und ihre Glyceriden gehören, hat grösseren Wert als 2. Ausserdem verhält sich K nicht immer strikt temperaturunabhängig: der K-Wert von Wasser, Ameisensäure z. B. wächst mit steigender Temperatur an, während sich der K-Wert von Tetrachlorkohlenstoff, Azeton und den meisten hochmolekularen Verbindungen mit steigender Temperatur vermindert. Die Ansicht, dass die Moleküle der Flüssigkeiten, deren K-Wert in der Nähe von 2 liegt, normal d. h. nicht assoziert seien, wird meistenteils als berechtigt angesehen. Die Ansicht, dass die Moleküle, deren K-Wert kleiner als 2 ist, assoziert seien, bewährt sich in einigen Fällen (z. B. bei Wasser, Essigsäure, Äthylalkohol), aber in einigen andern Fällen (z. B. bei Wasserstoff, Helium, geschmolzenen Metallen und Salzen) nicht. Der Schluss, dass die Moleküle der Flüssigkeiten, deren K-Wert grösser als 2 ist, dementsprechend dissoziert seien, wird offenbar widerlegt, da sie sich sonst normal verhalten. Die Ansicht, welche die Abweichung des K-Wertes von dem normalen Wert der Assoziation oder Dissoziation zuschreibt, hat also viel an Allgemeingültigkeit verloren.

Die erste molekularkinetische Grundlage des Eötvösschen Gesetzes verdankt man Madelung[50] und gleichfalls Born und Courant.[51] Die letzt genannten Autoren übertrugen auf die Moleküle in der Oberflächenschicht

(47) Walden, *Z. physik. Chem.*, **65** (1908), 129, 257, usw.
(48) Morgan, *Z. physik. Chem.*, **65** (1908), 851, usw.
(49) Jaeger, *Akad. Amsterdam Versl.*, **23** (1914); *Z. anorg. allg. Chem.*, **101** (1917), 1.
(50) Madelung, *Physik. Z.*, **14** (1913), 729.
(51) Born u. Courant, loc. cit. unter (43).

der Flüssigkeit die Betrachtungen, die zuerst von Debye[52] auf die Moleküle fester Körper angewandt wurden, und sie gelangten zu einer mit der Eötvösschen Formel gleichdeutigen Formel, wo sich der Zahlenwert von K unter bestimmten Voraussetzungen ableiten lässt. Sie konnten auch den abnorm grossen Wert von K für hochmolekulare Verbindungen dadurch deuten, dass die grossen Moleküle dieser Substanzen nicht bloss als Ganze schwingen, sondern dass im Molekül vorhandene Atomgruppen bestimmte Schwingungsfreiheit haben. Brillouin[53] verfeinerte die Born-Courantsche Theorie, indem er in der Flüssigkeitsoberfläche einen dem Lichtdruck analogen Druck annahm. Inzwischen hat die Langmuir-Harkinssche Theorie der Orientierung von Molekülen entwickelt.[54] Der Umstand, dass die Orientierung und Gestalt von Molekülen mit der Abweichung des K-Wertes vom normalen Wert im Zusammenhang stehe, wurde besonders von Adam[55] in Betracht gezogen. Adam hat dabei das Eötvösschen Gesetz in der Zustandsgleichung:

$$\Pi\omega = kT \tag{14}$$

wiedergegeben, indem er den Begriff des Oberflächendruckes einführte.

Die elektrische Theorie der Oberflächenschicht ist von Frenkel[56] und Jung[57] entwickelt worden. Jung hat die Eötvössche Formel abgeleitet, unter Zugrundelegung der Annahme, dass sich die Moleküle an der Oberfläche orientieren und dadurch ein inneres Feld entsteht. Es zeigt sich dabei, dass der K-Wert nur bei Substanzen mit sehr kleinem Dipolmoment temperaturunabhängig ist, während er bei Substanzen mit grossem Dipolmoment temperaturabhängig ist. Endlich wurde der Umstand, dass die mannigfaltig wirkenden Zwischenmolekularkräfte den Molekülverband beeinflussen und infolgedessen die komplizierte Temperaturabhängigkeit der Oberflächenspannung verursachen, hier und da nur andeutungsweise ausgesprochen.[58] Im folgenden soll gerade dieser letzt gennante Umstand, in bezug auf die oben angegebene Ableitung des Eötvösschen Gesetzes, besonders in Betracht gezogen werden. Die Betrachtungen bleiben übrigens mehr oder weniger formal, da unsere Kenntnisse über Molekularkräfte noch ungenügend sind.

(52) Debye, *Ann. Physik*, (4) **39** (1912), 789.
(53) Brillouin, loc. cit. unter (43).
(54) Langmuir u. Harkins, loc. cit.
(55) Adam, *Phil. Mag.*, (7), **8** (1929), 539.
(56) Frenkel, *Phil. Mag.*, (6), **33** (1917), 297; *Z. Physik*, **51** (1928), 232.
(57) Jung, *Z. physik. Chem.*, **123** (1926), 281.
(58) z. B. Freundlich, „Kapillarchemie," Bd. 1. (1930), S. 52; Adam, "The Physics and Chemistry of Surfaces," (1930), S. 158.

Wenn man die Eötvössche Formel in die Form :

$$\sigma\Omega = K(\vartheta_0 - T)$$

fasst, wobei

$$K = N^{\frac{2}{3}} k\left\{1 + \frac{\Phi(r)}{N^{\frac{2}{3}} k(\vartheta_0 - T)}\right\},$$

oder

$$K = 0.981\left\{1 + \frac{\Phi(r)}{N^{\frac{2}{3}} k(\vartheta_0 - T)}\right\}$$

ist, so folgen für K verschiedene mögliche Werte unter den Bedingungen :

1. $\Phi(r) > 0$

   a) $\Phi(r) > N^{\frac{2}{3}} k(\vartheta_0 - T)$, $1 + \dfrac{\Phi(r)}{N^{\frac{2}{3}} k(\vartheta_0 - T)} > 2$, $K > 2 \times 0.981$.

   b) $\Phi(r) = N^{\frac{2}{3}} k(\vartheta_0 - T)$, $1 + \dfrac{\Phi(r)}{N^{\frac{2}{3}} k(\vartheta_0 - T)} = 2$, $K = 2 \times 0.981$.

   c) $\Phi(r) < N^{\frac{2}{3}} k(\vartheta_0 - T)$, $1 < 1 + \dfrac{\Phi(r)}{N^{\frac{2}{3}} k(\vartheta_0 - T)} < 2$,
   $0.981 < K < 2 \times 0.981$.

2. $\Phi(r) < 0$

   a) $|\Phi(r)| < N^{\frac{2}{3}} k(\vartheta_0 - T)$, $0 < 1 + \dfrac{\Phi(r)}{N^{\frac{2}{3}} k(\vartheta_0 - T)} < 1$,
   $0 < K < 0.981$.

   b) $|\Phi(r)| = N^{\frac{2}{3}} k(\vartheta_0 - T)$, $1 + \dfrac{\Phi(r)}{N^{\frac{2}{3}} k(\vartheta_0 - T)} = 0$, $K = 0$.

   c) $|\Phi(r)| > N^{\frac{2}{3}} k(\vartheta_0 - T)$, $1 + \dfrac{\Phi(r)}{N^{\frac{2}{3}} k(\vartheta_0 - T)} < 0$, $K < 0$.

3. $\Phi(r) = 0$

   $1 + \dfrac{\Phi(r)}{N^{\frac{2}{3}} k(\vartheta_0 - T)} = 1$, $K = 0.981$.

Das Postulat 1) $\Phi(r) > 0$ bedingt zwischen den Molekülen die Anziehungskräfte. Die Konstante K wird dann nicht nur immer grössere Werte als 0.981, sondern auch verschieden grosse Werte annehmen, je nach dem möglichen Verhältnis der Kohäsionsenergie zur Differenz der statischen und thermischen Energie. Das Postulat 2) $\Phi(r) < 0$ bedingt dagegen die abstossenden Kräfte zwischen den Molekülen. K wird dabei kleiner als 0.981; er wird eventuell gleich null ausfallen. $K = 0$ fordert aber in der Eötvösschen Formel dass $\sigma = 0$ ist, sofern $T \neq \vartheta_0$ ist. Dass die σ, T-Gerade tatsächlich schon vor dem kritischen Punkt die T-Achse zu schneiden scheint, könnte also durch das Postulat 2) b) ermöglicht werden. Das Postulat 2) c) fordert $K < 0$ bzw. $\sigma < 0$, was aber in Wirklichkeit nicht möglich ist. Das letzte Postulat 3) $\Phi(r) = 0$ bedingt keine temperaturabhängigen Molekularkräfte zwischen den Molekülen, wo K einen bestimmten Wert, nämlich $N^{\frac{2}{3}}k = 0.981$ hat, sofern $T \neq \vartheta_0$ ist. Wenn nun die Temperatur gleich der kritischen Temperatur ist, so wird sowohl $\sigma = 0$ sein, als auch $\Phi(r) = 0$ sein (die erste Annahme). Dann wird K-Wert mathematisch anscheinend unbestimmt, sein Grenzwert wird aber null ergeben, wenn man die Bedingung:

$$\lim_{T \to \vartheta_0} |\Phi(r)| = \lim_{T \to \vartheta_0} N^{\frac{2}{3}} k(\vartheta_0 - T) = 0$$

als gültig annimmt. Schliesslich scheint es also erfolgreich den abnormen K-Wert mittels den Molekularkräften zu deuten, indem man den grössern K-Wert den Anziehungskräften und den kleineren K-Wert den Abstossungskräften zuordnet.

Nun war der abnorm kleine K-Wert von Wasserstoff, Helium, geschmolzenen Metallen und Salzen nicht begreiflich durch Assoziation und gerade in diesen Fällen hätte die Art des Molekülverbandes bzw. die Natur der Zwischenmolekularkräfte viel zu bedeuten. Es kommt wahrscheinlich zwischen Molekülen im flüssigen Wasserstoff oder Helium die van der Waalssche Kohäsion verhältnismässig nur in geringem Masse vor, wodurch der kleine K-Wert bei diesen Stoffen verständlich wird. Dagegen würden bei geschmolzenen Metallen und Salzen, in denen eher Atome oder Ionen existieren müssen, die abstossenden Kräfte zwischen ihnen zur Wirkung kommen, damit sich der noch viel kleinere K-Wert von diesen Substanzen verstehen lässt.

Der abnorme grosse K-Wert wäre den hohen Kohäsionskräften zwischen den Molekülen zuzuschreiben, was ja bei hochmolekularen Verbindungen im allgemeinen sehr wahrscheinlich ist. Man müsste aber bei hochmolekularen Verbindungen ausser den Zwischenmolekularkräften noch andere den K-Wert vergrössernd wirkende Faktoren, nämlich, Molekülzahl, Mole-

külgestalt, Molekularorientierung, Schwingungsfreiheit der Molekülgruppen usw. nennen. Der K-Wert ist dann eine recht komplizierte Funktion von diesen Faktoren, in denen die Zwischenmolekularkräfte immerhin als ein massgebender Faktor angesehen werden müssten.

Um sich davon noch besser zu überzeugen, betrachte ich unten die homologe Reihe der normalen Fettsäuren. Nach den Untersuchungen von Hunten und Maas[59] sind die K-Werte von den homologen Fettsäuren wie in folgender Tabelle:

Tabelle 6.

Stoff	K-Wert	$1-i$
Ameisensäure	0.90	0.00
Essigsäure	1.35	0.03
Propionsäure	1.53	0.15
Buttersäure	1.65	0.27
Capronsäure	2.04	0.57
Caprylsäure	2.12	0.54
Caprinsäure	2.36	0.65
Laurinsäure	2.56	0.77
Myristinsäure	2.80	0.79
Palmitinsäure	2.92	—
Margarinsäure	3.00	—
Stearinsäure	3.04	—

Der K-Wert wächst also beinahe regelmässig mit der sich vergrössernden Kettenlänge an. Auffallenderweise steht dieses Anwachsen in naher Analogie zu dem Anwachesen des $1-i$-Wertes bei den adsorbierten Schichten, der in der dritten Spalte zum Vergleich angegeben ist. (Teil I. Abs. 3) Sowohl das Anwachsen des $1-i$-Wertes durch die mit der Kettenlänge zunehmenden Dispersionskräfte lässt sich begreifen, als auch das Anwachsen des K-Wertes, welches durch dieselbe Kräfte erklärt werden könnte. Es müsste aber natürlich hierbei auch der Einfluss von Assoziation bzw. Molekülzahl, Molekülgestalt, Molekularorientierung und Molekülschwingung in Rücksicht gezogen werden. Der kleine Wert von K für Säuren bis die Kohlenstoffzahl 4 ist ja wahrscheinlich der Assoziation zuzuschreiben. Die Schwingungsfreiheit der Molekülgruppen könnte für alle Glieder als gleichmässig angenommen werden. Die Molekülgestalt und Molekularorientierung beeinflussen hierbei allerdings den K-Wert, indem sie ihn vergrössern, aber sie scheinen nicht imstande, das charakteristische Anwachsen vom K-Wert zahlenmässig wiederzugeben. So scheint es mir geglückt zu sein für diesen Fall den engen Zusammenhang des K-Wertes mit den Kohäsionskräften festzustellen.

Es wird nun auf die Veränderlichkeit des K-Wertes mit der Temperatur eingegangen. Der K-Wert in der Eötvösschen Formel ist eventuell recht konstant über einen grossen Bereich der Temperatur, aber er ist im allgemeinen nicht strikt unabhängig von der Temperatur und manchmal ver-

(59) Hunten u. Maas, loc. cit.

ändert sich der K-Wert auffallend mit der Temperatur. Der K-Wert von Wasser sowie von Essigsäure z. B. nimmt mit steigender Temperatur zu, wofür die Veränderlichkeit des Assoziationsgrades verantwortlich sein könnte. Auch der K-Wert von solchen normalen Substanzen wie Tetrachlorkohlenstoff, Äthylazetat und andern ist weitgehend temperaturabhängig, und zwar nimmt er mit steigender Temperatur ab. Dagegen haben hochmolekulare Verbindungen meist einen zu grossen und mit steigender Temperatur abnehmenden K-Wert. Bei anisotropen Flüssigkeiten verhält sich der K-Wert ganz charakteristisch; er wächst mit steigender Temperatur bis zu einem maximalen Wert an und dann vermindert er sich allmählich. Gerade in diesen Fällen hätte die Natur der Zwischenmolekularkräfte für die Temperaturabhängigkeit des K-Wertes viel zu bedeuten.

Die Veränderlichkeit des K-Wertes mit der Temperatur lässt sich nun auch aus der Zustandsgleichung (6) als ein natürlicher Schluss folgern. Rechnet man also die Zustandsgleichung:

$$\sigma\Omega = \sigma_0\Omega - N^{\frac{2}{3}}kT + \Phi(r)$$

auf die Flächeneinheit, so ergibt sich:

$$\sigma = \sigma_0 - n^{\frac{2}{3}}kT + \varphi(r)\,,$$

wo $\varphi(r)$ eine Funktion von Temperatur ist. Differenziert man dies nach T, so wird:

$$\frac{d\sigma}{dT} = -n^{\frac{2}{3}}k + \varphi'(r)\,.$$

Dies durch nochmalige Differentierung nach T, wird:

$$\frac{d^2\sigma}{dT^2} = \varphi''(r)\,.$$

Wenn also $\varphi''(r)$ gleich null wäre, so würde $\frac{d\sigma}{dT} = \text{constans}$, demnach würde $\frac{d(\sigma\Omega)}{dT}$ constans, d. h. die Eötvössche Konstante K temperaturunabhängig sein. Wenn aber sonst $\varphi''(r)$ nicht gleich null wäre, so würden folgende Möglichkeiten resultieren:

1) $\varphi''(r) > 0$ d. h. $\frac{d^2\sigma}{dT^2} > 0\,.$ (15)

2) $\varphi''(r) < 0$ d. h. $\frac{d^2\sigma}{dT^2} < 0\,.$ (16)

Der erste Fall bedingt, dass $\frac{d\sigma}{dT}$ mit steigender Temperatur zunimmt, dementsprechend der K-Wert mit steigender Temperatur abnimmt, während der zweite bedingt, dass $\frac{d\sigma}{dT}$ mit steigender Temperatur abnimmt, dementsprechend der K-Wert gleichzeitig zunimmt.

Nun stellt $\sigma\Omega$ die freie molare Oberflächenenergie dar. Bezeichnet man mit U die gesamte molare Oberflächenenergie, so gilt die thermodynamische Beziehung:

$$U = \sigma\Omega - T\frac{d\sigma}{dT}\Omega \,, \tag{17}$$

und für die Oberflächeneinheit:

$$u = \sigma - T\frac{d\sigma}{dT} \,. \tag{18}$$

Differentiert man dies nach T, so bekommt man:

$$\frac{du}{dT} = -T\frac{d^2\sigma}{dT^2} \,. \tag{19}$$

Aus Gleichung (18) lässt sich auch folgern:[60]

$$\frac{dc_v}{d\omega} = -T\frac{d^2\sigma}{dT^2} \,, \tag{20}$$

wo c_v die spezifische Wärme der Flüssigkeit bei konstantem Volum bedeutet. Kombiniert man diese Beziehungen (19), (20) mit den Bedingungen (15), (16), so werden:

1) $\varphi''(r) > 0$, $\frac{d^2\sigma}{dT^2} > 0$, $\frac{du}{dT}$, $\frac{dc_v}{d\omega} < 0$,

K nimmt mit der Temperatur ab.

2) $\varphi''(r) < 0$, $\frac{d^2\sigma}{dT^2} < 0$, $\frac{du}{dT}$, $\frac{dc_v}{d\omega} > 0$,

K nimmt mit der Temperatur zu.

Hochmolekulare Verbindungen wie z. B. Triolein, Tripalmitin gehören zu dem ersten Fall, während Ameisensäure, Wasser, Phenol und andere zu dem zweiten Fall gehören.

(60) Dupré, *Ann. chim. phys.*, (4), **11** (1867), 200.

Je nachdem der K-Wert mit steigender Temperatur zunimmt oder abnimmt, verläuft die $\sigma\Omega$, T-Kurve konkav oder konvex nach der T-Achse. Fig. 7 zeigt eine schematische $\sigma\Omega$, T-Kurve, eine solche wird in der Tat von Stoff zu Stoff gefunden werden.

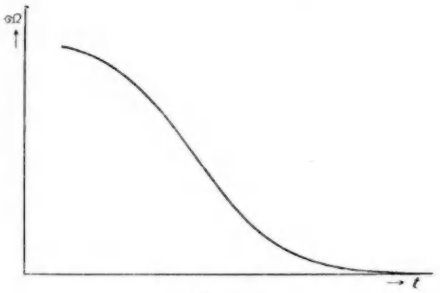


Fig. 7.

Bei hohen Temperaturen würden in den meisten Fällen zwischen Molekülen abstossende Kräfte hervorkommen ($\varphi(r) < 0$), und wenn in der Nähe der kritischen Temperatur die Bedingung:

$$|\varphi(r)| = n^{\frac{2}{3}} k(\vartheta_0 - T) ,$$

infolgedessen:

$$\frac{d\sigma}{dT} = -n^{\frac{2}{3}} k - \varphi'(r) = -n^{\frac{2}{3}} k + n^{\frac{2}{3}} k = 0$$

gilt, so wird die $\sigma\Omega$, T-Kurve sich asymptotisch der T-Achse nähern bis sie schliesslich auf die T-Achse fällt, wo

$$\sigma = 0 , \quad K = 0 \quad \text{und} \quad \frac{d\sigma}{dT} = 0 \quad \text{ist.}$$

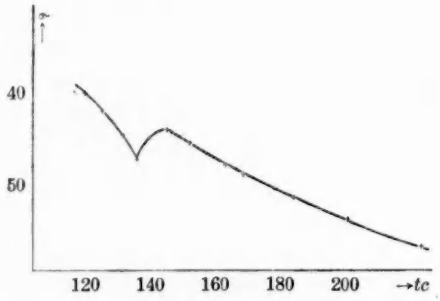
(Siehe Fig. 7.)

3. Über das abnorme Verhalten der anisotropen Flüssigkeiten.

Bei gewöhnlichen Flüssigkeiten kann K-Wert keineswegs negativ sein, denn, wenn er negativ wäre, so würde σ in Gleichung (9) negativ ausfallen, sofern $T < \vartheta_0$ ist, was aber allerdings unrealisierbar ist. Dagegen kann der K-Wert bei anisotropen Flüssigkeiten[61] (eventuell bei geschmolzenen Metallen, insbesondere Cadmium[62]) negativ ausfallen d. h. die Oberflächenspannung dieser Stoffe steigt mit der zunehmenden Temperatur an, im schmalen Temperaturbereich, wo sich die Flüssigkeit von anisotrop zu isotrop umwandelt. Eine deratige Ansteigung der σ, T-Kurve findet man tatsächlich in Fig. (8), (9), (10) und (11) (gezeichnet nach den Versuchen von Jaeger).[61] Überdies sieht man dort den ganzen Verlauf der σ, T-Kurve,

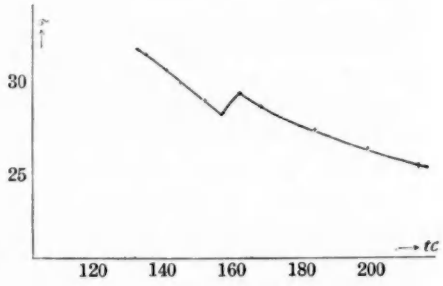
(61) Jaeger, *Z. anorg. allg. Chem.*, **101** (1917), 1.
(62) Bircumshow, *Phil. Mag.*, (7), **3** (1927), 1291.

der uns viel Charakteristisches zeigt. Wie dies zustandekommt, soll unten erläutert werden.



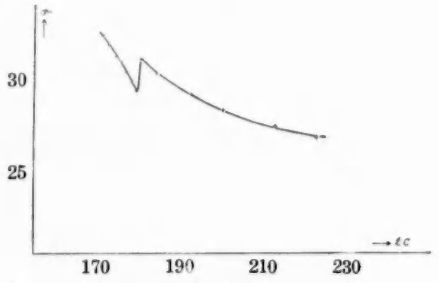
p-Azoxyanisol

Fig. 8.



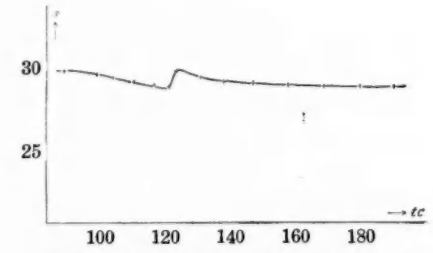
p-Azoxyphenetol

Fig. 9.



Anisaldazin

Fig. 10.



p-Alloxybenzalamino-α-Methylzimtsäure-Äthylester

Fig. 11.

Auch für die Oberflächenschicht der anisotropen Flüssigkeiten stelle ich die zweidimensionale Zustandsgleichung auf, und zwar in die Form:

$$\sigma\Omega = N^{\frac{2}{3}} k(\vartheta^* - T) + \Phi(r) , \qquad (21)$$

wo ϑ^* nicht mehr die kritische Temperatur, sondern die Umwandlungstemperatur (anisotrop $\rightleftarrows$ isotrop) darstellt. Nun wird die Oberflächenspannung der anisotropen Flüssigkeiten bei $T = \vartheta^*$ nicht gleich null, und so folgt aus Gleichung (21) für $T = \vartheta^*$:

$$\sigma^*\Omega = \Phi^*(r) , \qquad (22)$$

oder für die Flächeneinheit:

$$\sigma^* = \varphi^*(r) \,, \qquad (23)$$

wo * den Wert beim Umwandlungspunkt charakterisiert. Diese Beziehung besagt: Die Oberflächenspannung ist bei dem Umwandlungspunkt gleich dem temperaturabhängigen Bestandteil der Kohäsionsenergie (pro Flächeneinheit).

Im Umwandlungspunkt steht die anisotrope Flüssigkeit mit der isotropen Flüssigkeit im Gleichgewicht, die letztere aber hätte ein grösseres inneres Potential als die vorige. Also würde gelten:

$$\varphi^{**}(r) > \varphi^*(r) \,, \qquad \text{oder} \qquad \sigma^{**} > \sigma^* \,,$$

wo $\varphi^{**}(r)$ die Kohäsionsenergie und σ^{**} die Oberflächenspannung der isotropen Flüssigkeit, die mit der anisotropen im Gleichgewicht steht, bedeutet. Die grössere Oberflächenspannung der isotropen Flüssigkeit könnte ja nach der Schwärmetheorie von Ornstein und Kast[63] erwartet werden, da die orientierten Schwärme bei der Umwandlung (anisotrop → isotrop) abgebaut werden, indem die ungesättigten aktiven Gruppen im Molekül an der Oberfläche entblösst werden und daraus die Vermehrung der Oberflächenspannung resultiert.

Tatsächlich tritt aber die Umwandlung meist nicht ganz scharf in einem Punkt ein, sondern in einem kleinen Bereich der Temperatur, dementsprechend steigt die Oberflächenspannung ziemlich steil von einem minimalen Wert zu einem maximalen an (Fig. 8–11), während sich die Flüssigkeit von anisotrop zu isotrop umwandelt. Sobald die Flüssigkeit isotrop ist, nimmt die Oberflächenspannung, wie bei gewöhnlichen Flüssigkeiten, mit steigender Temperatur allmählich ab.

Charakteristisch ist die ganze Gestalt der σ, T-Kurve der flüssigen Kristalle. Die σ, T-Kurve verläuft anfänglich konkav nach T-Achse (der K-Wert nimmt mit steigender Temperatur zu) und beim Umwandlungspunkt steigt die σ, T-Kurve senkrecht zur T-Achse an (der K-Wert wird dabei unendlich gross) und dann, wenn die Flüssigkeit isotrop ist, verläuft die Kurve konvex nach der T-Achse (der K-Wert nimmt mit steigender Temperatur ab.). Fig. 12 zeigt einen solchen idealen Verlauf, während Fig. 8–11 den wirklichen Verlauf bei p-Azoxyanisol, p-Azoxyphenetol, Anisaldazin und p-Alloxybenzalamino-α-Methylzimtsäure-Äthylester zeigen.

Wenn die Beziehung:

$$\sigma^* = \varphi^*(r)$$

(63) Ornstein u. Kast, *Trans. Faraday Soc.*, **29** (1933), 931.

gültig ist, so wird die Kohäsionsenergie beim Umwandlungspunkt aus Daten der Oberflächenspannung berechnet werden. Man betrachtet hier insbesondere *p*-Azoxyanisol und *p*-Azoxyphenetol, deren langgestreckte Moleküle um eine in der Mitte befindliche polare Gruppe symmetrisch gebaut sind. Diese Moleküle haben wahrscheinlich in der smektischen Mesophase eine solche Anordnung etwa nach dem Schema wie Fig. 13 zeigt (nach Ebert und

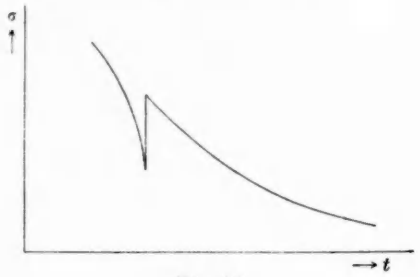


Fig. 12.

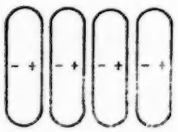


Fig. 13.

v. Hartel[64]), indem der Vektor des elektrischen Dipolmomentes von Molekülen parallel der ausgezeichneten Achse liegt, so dass sich die entgegengesetzt geladenen Pole entsprechend aneinander hängen können.

Wenn man hier die richtenden Molekularkräfte in erster Annäherung auf die statischen Dipolkräfte zurückführen könnte, so würde folgende Beziehung entstehen:

$$\Phi^*(r) = -N^{\frac{2}{3}}kT\frac{B}{\Omega} = \frac{N^{\frac{4}{3}}\pi}{2\Omega}\int_{r_0}^{\infty} r^2\frac{\partial E}{\partial r}e^{-\frac{E}{kT}}dr\,.$$

Setzt man hierfür

$$E = \frac{2\mu^2}{r^3}$$

ein, so wird:

$$\Phi^*(r) = -\frac{N^{\frac{4}{3}}\pi}{2\Omega}\int_{r_0}^{\infty} r^2\frac{6\mu^2}{r^4} = -\frac{3N^{\frac{4}{3}}\pi\mu^2}{\Omega}\int_{r_0}^{\infty}\frac{1}{r^2}dr = \frac{3N^{\frac{4}{3}}\pi\mu^2}{\Omega r_0}\,,$$

wo r_0 den kleinsten Abstand der Dipolzentren bedeutet. Dies in Beziehung (22) eingesetzt, ergibt:

$$\sigma^*\Omega = \frac{3N^{\frac{4}{3}}\pi\mu^2}{\Omega r_0}\,,$$

oder

(64) Ebert u. v. Hartel, *Physik. Z.*, **28** (1927), 786.

$$\mu^2 = \frac{\sigma^* \Omega^2 r_0}{3\pi N^{\frac{4}{3}}} = \frac{\sigma^* r_0}{3\pi}\left(\frac{M}{\rho N}\right)^{\frac{4}{3}},$$

wo M das Molargewicht und ρ die Dichte bedeutet. Hier sind M, σ und ρ bekannt, somit, wenn man für r_0 einen wahrscheinlichen Wert annimmt, wird das Dipolmoment μ daraus berechnet werden.

Für *p*-Azoxyanisol:

$$M = 258, \quad \vartheta^*(\mathrm{C}) = 129.5^\circ, \quad \sigma^* = 36.4 \text{ Dyn/cm},$$

$$\rho = 1.159, \quad r_0 = 4 \times 10^{-8} \text{ cm}: \quad \mu_{\text{ber.}} = 2.28 \times 10^{-18} \text{ E.S.E.}$$

Für *p*-Azoxyphenetol:

$$M = 286, \quad \vartheta^*(\mathrm{C}) = 164^\circ, \quad \sigma^* = 28.3 \text{ Dyn/cm},$$

$$\rho = 1.07, \quad r_0 = 4 \times 10^{-8} \text{ cm}: \quad \mu_{\text{ber.}} = 2.26 \times 10^{-18} \text{ E.S.E.}$$

Die Dipolmomente dieser Substanzen wurden von Ebert und v. Hartel[65] dielektrisch gemessen: $\mu = 2.3 \times 10^{-18}$ für *p*-Azoxyanisol, $\mu = 2.24 \times 10^{-18}$ für *p*-Azoxyphenetol. Die berechneten Dipolmomente stehen also mit den beobachteten Dipolmomenten in vorzüglicher Übereinstimmung.

Die Bornsche Theorie[66] der flüssigen Kristalle ist von Ebert und v. Hartel kritisiert worden. Über die Verwendbarkeit der Bornschen Betrachtungen über die flüssigen Kristalle auf die orientierten Oberflächenschichten habe ich im Anschluss an die Jungsche Arbeit[67] schon in meiner vorhergehenden Bericht kurz diskutiert.[68]

Zusammenfassung.

Im Hinblick auf die grosse Bedeutung der Grenzflächenerscheinungen ist es wünschenswert eine allgemeine Theorie und eine Systematik zu geben. Dies ist uns zum minderstens für die Grenzfläche flüssig-gasförmig gelungen, sei es die Oberflächenschicht reiner Flüssigkeiten oder die adsorbierte Schicht, indem man für die Schicht unter besonderer Berücksichtigung der Zwischenmolekularkräfte eine allgemeine zweidimensionale Zustandsgleichung aufstellt.

(65) Ebert u. v. Hartel, loc. cit.
(66) Born, *Ann. Physik*, **55** (1918), 222.
(67) Jung, loc. cit.
(68) Tamamushi, Dieses Bulletin, **6** (1931), 207.

1. Die Zustandsgleichung der adsorbierten Schicht wurde mittels der Virial-Methode abgeleitet.

2. Mit Hilfe der Zustandsgleichung der adsorbierten Schicht wurden Adsorptionsgleichungen, insbesondere die Adsorptionsisotherme von Langmuir und diejenige von Freundlich, thermodynamisch hergeleitet.

3. Die theoretisch hergeleiteten Beziehungen wurden mit den empirischen Daten, die besonders für die homologe Reihe der normalen Fettsäuren gewonnen sind, verglichen.

4. Es wurden Überlegungen über die Natur der lateralen Kohäsionskräfte bei den Fettsäuren angestellt. Die Kohäsionskräfte wurden zum Teil dem elektrostatischen Effekt und zum anderen Teil dem quantenmechanischen Effekt zugeschrieben. Der letzt genannte Effekt erklärte das Anwachsen der Kohäsion mit der Kettenlänge der Moleküle. Es wurde auf die Rolle der lateralen Kohäsion bei der Strukturbildung der adsorbierten Schicht hingewiesen.

5. Es wurde eine Deutung der Traubeschen Regel angegeben. Dass die Traubesche Regel auch in verdichteten Schichten, wo die parallele Orientierung von Molekülen von keiner Seite angezweifelt wird, gültig ist, wurde durch solchen Mechanismus bestätigt, dass die Kohlenwasserstoffketten infolge der zwischen ihnen wirkenden Molekularkräfte aus dem Innern der Lösung zur Oberfläche um so kräftiger herausgedrängt werden, je länger sie sind.

6. Es wurde für die Oberflächenschicht reiner Flüssigkeiten die zweidimensionale Zustandsgleichung aufgestellt.

7. In dieser Zustandsgleichung wurde die Oberflächenspannung als Summe dreier Energien d. h. der rein statischen Kohäsion, der Temperaturbewegung und der temperaturabhängigen Zwischenmolekularkräfte angegeben. Die Gleichung gab also eine Definition der Oberflächenspannung. Aus derselben Gleichung wurde die Eötvössche Formel $\sigma = K(\vartheta_0 - T)$ abgeleitet, wo K nicht eine einfache Konstante, sondern eine Funktion darstellt, die im allgemeinen von Stoff zu Stoff verschieden und auch von der Temperatur abhängig sein muss. Der abnorme kleine oder grosse K-Wert, besonders bei solchen Stoffen, wo das Zustandskommen von Assoziation sowie Dissoziation unwahrscheinlich ist, wurde auf die zwischen Molekülen in verschiedenem Mass wirkenden abstossenden oder anziehenden Molekularkräfte zurückgeführt. Die Ansteigung des K-Wertes bei der Verlängerung der Kette in den Fettsäure-Molekülen wurde mit der gleichzeitigen Zunahme der Kohäsionskräfte in Zusammenhang gebracht.

8. Auf das abnorme Verhalten der anisotropen Flüssigkeiten wurde besonders eingegangen. Es wurde eine Erklärung über den charakteristischen Verlauf der σ, T-Kurve dieser Stoffe angegeben. Das Dipolmoment

von *p*-Azoxyanisol und von *p*-Azoxyphenetol wurde näherungsweise berechnet, unter der Voraussetzung, dass die Oberflächenspannung beim Umwandlungspunkt anisotrop ⇄ isotrop den temperaturabhängigen Kohäsionskräften gleich ist.

Herrn Prof. Dr. M. Katayama möchte ich an dieser Stelle für die Anregungen und die Ratschläge, mit der er in zuvorkommendster Weise meine Arbeit gefördert hat, meinen verbindlichsten Dank aussprechen.

Musashi Hochschule,
Itabashiku, Tokio.

ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. VIII. THE RELATION BETWEEN THE CATALYTIC ACTIVITY AND THE ADSORPTION.*

By Koshiro ISHIMURA.

Received July 26th, 1934. Published November 28th, 1934.

In the previous paper[1] the behaviours of the chief constituents of Japanese acid earth in the catalytic action on naphthalene have been elucidated, and it has been noted that there exists the parallelism between their chemical compositions and catalytic activities. The present paper deals with the relation between their catalytic activities and adsorptive powers. The specimens of the acid earth used in the present investigation are the same as those mentioned in the previous paper and their general descriptions are here omitted.

The adsorptive power of the acid earth greatly depends upon the nature of adsorbates, i. e. upon their acidities or basicities, and therefore the catalytic activity on naphthalene was compared with adsorptive powers for neutral substances such as water, benzene, and naphthalene itself.

From the experiments described below on the adsorption of the various specimens of the acid earth for these neutral substances, it is concluded that the larger the surface area the greater is the catalytic activity. Therefore,

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* An epitomized translation of the original published in Vol. 29 of the Reports of the Tokyo Imperial Industrial Research Laboratory.

(1) Inoue and Ishimura, This Bulletin, **9** (1934), 431.

if the catalysis does not take place on the whole surface uniformly but only on some particular parts, the active centres, then the distribution of these active centres on the surface is approximately equal for the various specimens of the acid earth, that is, the magnitude of the catalytic activity depends upon the surface area possessing active centres equally distributed but not on the number of the active centres on the equal surface area. On the other hand, the catalytic activity is closely connected with the chemical composition, as stated in the previous paper, so it may not be illogical to consider that the surface area is influenced by the chemical composition; the larger the ratio Al_2O_3/SiO_2 and the smaller the ratio $CaO+K_2O/SiO_2$, the greater is the surface area.

The Adsorption of Water. Six specimens of the earth were taken. Each of them was dried at 120°, powdered, and particles with mesh-size of 60–80 were sifted out, about 0.5 g. of which were taken into the weighing bottle, and heated at 300° in an electric furnace to a constant weight. The bottle was then put on a glass stand placed in a wide-necked bottle containing some distilled water in a thermostat of 25°. It was taken out at intervals and weighed. The amount of adsorbed water is plotted against time in Fig. 1. The letters assigned to the samples denote their order of the magnitude of the catalytic activity, earth A having the smallest activity and earth G the greatest as noted in the previous paper. Fig. 1 shows that a parallelism holds between the catalytic activity and both the adsorption velocity and capacity up to about 20 per cent. of water adsorbed.

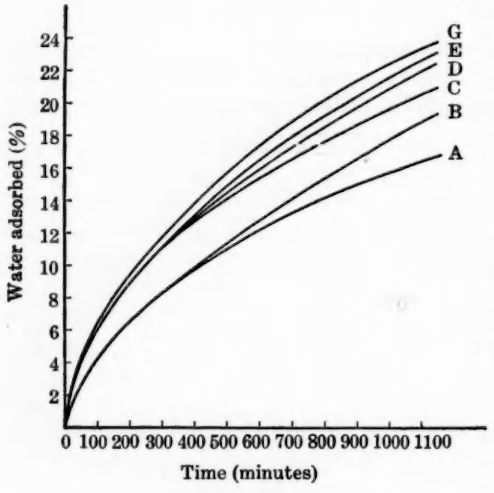

Fig. 1.

Adsorption velocity depends upon both the surface area and adsorption intensity, and so if adsorption intensity is constant the surface area only influences the velocity. The adsorption intensities of the acid earths for water may be taken constant after the whole surfaces are covered with several

layers of water molecules. Since the amount of water sufficient to cover the whole surface of the earth in a monomolecular layer is about 2.5 per cent. of the weight of the dry earth, as will be shown in later communications, the adsorption intensities of the various specimens of the earth may be safely taken as constant after the amount of water several times as great as the above value has been adsorbed. However, the monomolecular film of water is not necessarily formed on the whole surface before the formation of any polymolecular layer begins[2] and, moreover, it cannot be admitted that layer adsorption only takes place all over the surface before there occurs capillary condensation even in the early stage of the adsorption under the experimental condition above mentioned. Yet if it is assumed that the distribution of radii of pores is of approximately the same probability for all specimens of the acid earth, then the adsorbed amount within certain limits can be regarded as collected on the surface by layer condensation only with a constant intensity, and therefore their adsorption velocities for water depend upon the surface areas only and the adsorbed amounts within those limits can be taken as measures of the surface areas, when the various specimens of the acid earth are taken into consideration in comparison with one another. Therefore it seems that the curves given in Fig. 1 can be interpreted as showing that the larger the surface area the greater is the catalytic activity.

The Adsorption of Benzene. The integral heats of wetting of the various specimens of the acid earth in benzene were compared by the method proposed by Berl and Andress[3] who have shown that the integral heats of wetting of porous materials such as active charcoals and silica gels can be taken as measures of their adsorptive powers and that ether isotherms for various charcoals are practically quantitatively related to the heats of wetting in benzene. The apparatus and manipulation were practically the same as those of Berl and Andress. The double wall was formed with two test-tubes of different sizes and a rubber stopper, and pure benzene (d_4^{25}, 0.8731) (10 c.c.) was poured into the inner tube fitted with a thermometer graduated to 0.1°. After the temperature became constant for about 5 minutes, the earth (sifted by a 200 mesh sieve and dried at 300° for one hour) (3.00 g.) was weighed out and rapidly put into the benzene, the thermometer being lifted meanwhile, and then serving as a stirrer. The change of temperature was recorded at the interval of one minute to 0.01°. In every case

(2) In fact, the experiments to be described in the next communication seem to indicate that there remain some parts uncovered on the surface even in the neighbourhood of saturation.

(3) *Z. angew. Chem.*, **35** (1922), 722;

the mercury thread climbed to a maximum position within one minute and then gradually fell down. The sum of the rise and fall at the ends of the first two minutes was taken as a measure of the heat of wetting as proposed by the German authors. It is necessary to start each experiment at temperature not so different in order to keep all such heat measurements comparable. The results are shown in Table 1. In the fourth column, the catalytic activities on naphthalene measured by the yields of resinous matter are cited from the previous paper.[4]

Table 1.

Earths	Temperature changes	Means	Yields of resinous matter (g.)
A	0.84 0.89	0.87	1.65
B	1.53 1.57	1.55	1.82
C	1.71 1.74	1.73	1.86
D	1.71 1.93	1.82	1.90
E	2.38 2.19	2.29	2.10
F	2.63 2.66	2.65	2.23
G	2.87 2.59	2.73	2.60

The above results are quite analogous to those shown in Fig. 1; the catalytic activity goes parallel with the heat of wetting.

The heat evolved when solid is wetted by liquid is due to some surface phenomenon, but it is hardly conceivable that when liquid is stored in large pores it would give rise to the heat effect of measurable magnitude, hence the heat of wetting may be a function of both the intensity and capacity factors of adsorption,—whether it is the layer adsorption or the condensation in capillaries of molecular size or both—but not a function of the saturation capacity. A number of papers[5] have been published which show that the heat of wetting is a function of the surface area. It seems, however, that there must be an implied assumption that the surface is homogeneous or if heterogeneous there is no appreciable difference in the heat effect between the active and inactive parts[6] or, if any, it is negligible compared with the total heat evolved. The catalytically active parts on the surface of solid catalysts represent generally very small fraction of the total surface area[7] and

(4) Loc. cit.

(5) Macy, *J. Phys. Chem.*, **34** (1931), 1397; Berl and Burkhardt, *Z. angew. Chem.*, **43** (1930), 332; Bartell and Fu, *Colloid Symposium Annual*, **7**, 135.

(6) Lamb and Coolidge found that the heats of adsorption of vapours are very nearly equal on inactive as on active charcoals of the same kind (*J. Am. Chem. Soc.*, **42** (1920), 1146).

(7) Rideal and Wright, *J. Chem. Soc.*, **127** (1925), 1352; Hoover and Rideal, *J. Am. Chem. Soc.*, **49** (1927), 122; Garner, Mckie and Knight, *J. Phys. Chem.*, **31** (1927), 644.

therefore even if the heat evolved on the adsorption of molecules directly held on these particular parts be much greater than on other parts or than of molecules localized on the upper parts of the adsorbed layers, their effect may be very small compared with the total heat quantity. Therefore the heat of wetting in general may be taken as an approximate measure of the surface area for the same kind of catalysts.

Thus the same conclusion may be attained from Table 1 that the larger the surface area the greater is the catalytic activity of the acid earth.

The values of the heat of wetting fall considerably as the drying temperature of the acid earth is raised. The temperature change due to the heat of wetting measured by the above-mentioned method is plotted against the drying temperature of earth F in Fig. 2. Each sample was dried at the required temperature for one hour. There may occur the sintering of catalyst mass causing the diminution of the surface area as temperature rises, yet at the same time more severe change of the surface may take place with the liberation of water, the nature of the acid earth thereby suffering the fundamental change as believed by many authors.[8]

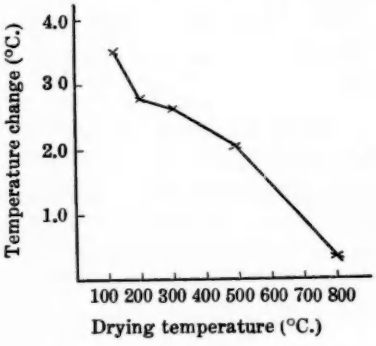

Fig. 2.

The heats of wetting of various materials other than the acid earth were compared by the same method. All of the samples are the same as those described in the previous paper.[9] The data are tabulated in Table 2,[10] in which the catalytic activities are also quoted from the previous paper.

It would be impossible to compare the surface areas of these substances of widely different natures by the heats of wetting, because their adsorption intensities for benzene would be greatly different from one another, though it is noticed that such substances as active charcoal and silica gel generally accepted as of very large surface areas evolve the larger heat quantities. There can be denoted no relationship between the heat of wetting and the catalytic activity given in Table 2.

(8) Kobayashi, Yamamoto and Bito, *J. Soc. Chem. Ind. Japan*, **32** (1929), 298B; Kameyama and Oka, ibid., **32** (1929), 94B; Isobe, *Sci. Papers of Inst. Phys. Chem. Research, Japan*, **14** (1930), 229.

(9) Loc. cit.

(10) In case of voluminous substances such as active charcoal and diatomaceous e rth 1.5 g. were taken and the observed values of the temperature change were doubled.

Table 2.

Subst.	Earth F	Earth F treated with HCl	Bento-nite	Bento-nite treated with HCl	Cao-line	Clay I	Dia-tom. earth	Bau-xite	Ac-tive char-coal	Silica gel a	$Al(OH)_3$ b
Temp. Change	2.65	3.18	2.93	2.11	0.45	1.02	0.91	5.13	6.80	6.60	4.57
Yields of resi-nous matter	2.23	2.33	0.25	2.89	0.81	0.33	0.22	0	0	0.03	0.02

As for bentonite, the surface area suffers little change by the treatment with hydrochloric acid, while its catalytic activity is increased greatly owing to the removal of poisons from the surface as suggested in the previous publication. In the case of the acid earth, its chemical composition and consequently its catalytic activity as well as its surface area is increased by a small degree by the same treatment.

The Adsorption of Naphthalene. Naphthalene has a very small vapour pressure at ordinary temperature and it will take a very long time for it to saturate adsorbents, while the complication of the apparatus and the difficulty of manipulation would be accompanied in experiments at high temperatures. A rigorous temperature regulation is not needed in the present experiment, since what is required is not the correctness of values but only relative adsorptive powers. So the experiment was carried out at room temperature as follows. About 0.5 g. of each acid earth (sifted by a 200 mesh sieve and dried at 300° for one hour) is weighed in a weighing bottle of the same size, put in a desiccator of sulphuric acid ($d = 1.84$), and left to stand for 7 days, and then a dish containing naphthalene, dried beforehand on sulphuric acid of the same specific gravity, is placed at the centre of the desiccator. Naphthalene is slowly adsorbed by the earth. The weighing bottle is taken out at intervals and weighed. The amount adsorbed is plotted against time as shown in Fig. 3. The increase or decrease in the weight of the earth due to the difference between the vapour pressure of the acid earth and that of sulphuric acid is negligible as a blank test has shown.

The magnitude of the surface area of the acid earth is of the order of about 10 square metres per gram as will be shown in later communication and it is very probable that the adsorbed naphthalene forms a monomolecular

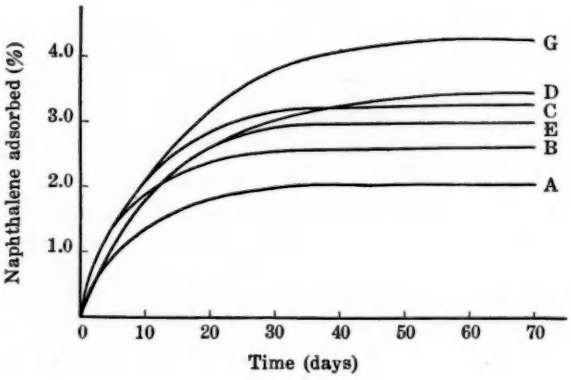

Fig. 3.

film on the surface,[11] if its molecular dimensions and the amounts adsorbed by the acid earths are taken into consideration.[12] Therefore, the surface areas of the earths may be roughly measured by the saturation capacities for naphthalene. Fig. 3 shows that the surface area goes parallel with the catalytic activity (with one exception of the earth designated E). Thus the author has come here again to the same conclusion.

As has been stated in the previous paper, the catalytic activity is almost entirely destroyed by the addition of about 3 per cent. of sodium hydroxide or lime. The surface area and consequently the amount of adsorbed naphthalene, however, will not change greatly as long as pores are not blocked up by the added matter. If, on the contrary, the amount added is large enough to block up some of small pores, then the diminution of the surface will occur, manifested by the decrease in the amount of adsorbed naphthalene. Plots given in Figs. 4 and 5 are in close agreement with the above speculation. There are three breaks in every curve, which seems to be unavoidable under the experimental condition mentioned above, since the temperature of the laboratory and the vapour pressure of naphthalene rose gradually as the experiment extended from the 8th of December, 1930, to the 4th of April, 1931.

(11) It is improbable, however, that a perfect monomolecular film is always formed, for in the course of the adsorption of naphthalene the colour of the earths turns gradually from light yellow to brownish black, indicating that at room temperature there occurs already the catalytic action.

(12) The dimensions of naphthalene molecule are 8.68 by 6-7 by 3×10^{-8} cm. (Adam, The Physics and Chemistry of Surfaces, 1930, p. 95). A calculation shows that the area to be covered by 0.02 g. of naphthalene is 17.0-58.8 square metres according to the orientation of the molecules on the assumption of a packed monomolecular layer.

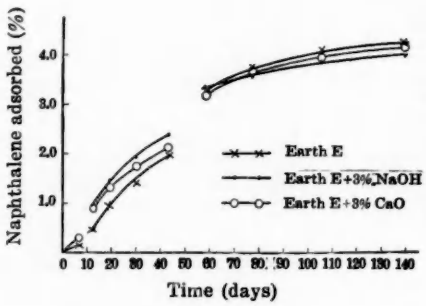

Fig. 4.

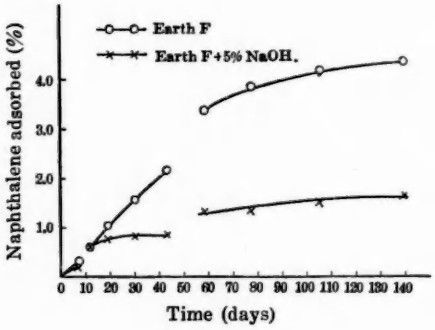

Fig. 5.

Fig. 6 shows the curves of the adsorbed amount plotted against time for several substances together with that for earth F. The substances are the same as those given in Table 2. The amount adsorbed by active charcoal is about ten times as great as that by the earth, and the surface of the

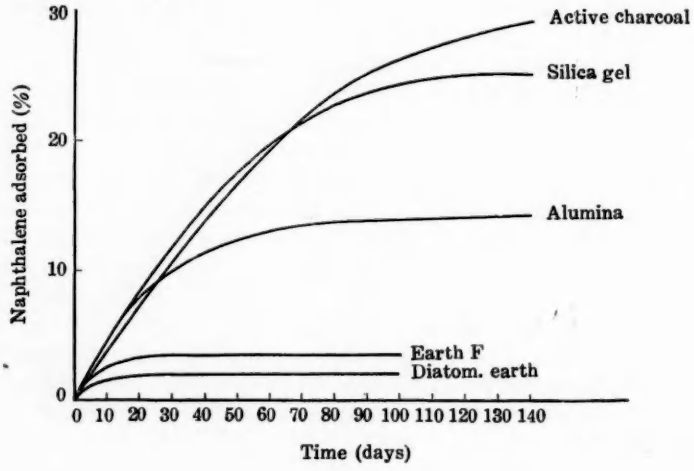

Fig. 6.

former is also about ten times as large as that of the latter, as will be shown in later paper. It is very probable therefore that the surface areas of several materials of widely different natures also can be compared with one another by the saturation capacities for naphthalene. A close parallelism is observed also between the data given in Table 2 and Fig. 6.

Summary.

(1) The catalytic activity of Japanese acid earth on naphthalene has been compared with its adsorptive powers for water, benzene, and naphthalene.

(2) The relations between the adsorptive powers and the surface area of the earth have been discussed.

(3) It has been concluded that the larger the surface area the greater is the catalytic activity and therefore the magnitude of the catalytic activity depends upon the surface area possessing active centres equally distributed but not on the number of the active centres on the equal surface area.

(4) The influence of the chemical composition of the earth on its surface area has been suggested.

The author is very grateful to Dr. Inoue for helpful advice and criticism.

The Tokyo Imperial Industrial Research Laboratory,
Hatagaya, Tokyo.

ON THE VAPOUR-PHASE HYDROLYSIS.

By Shigeaki YAMASAKI and Toshizo TITANI.

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There have been a great many investigations on the reactions of organic compounds with water, particularly in connection with the hydrolysis of esters in aqueous solutions. All these results have brought about a number of theories regarding the mechanism of the reaction: the theory generally accepted states that the hydrolytic reaction occurs in two stages, the first being a rapid formation of a substrate-water complex and the second the subsequent reaction of the complex with hydrogen-ion to give final products of the hydrolysis.[1] For example, the hydrolysis of esters in aqueous solutions can be represented by the following scheme:

(1) Cf., for example, F.O. Rice, "The mechanism of homogeneous organic reactions," Chemical Catalog Co., 1928, 104.

$$\text{ester} + \text{water} \rightleftarrows \text{ester}\cdot\text{water},$$

$$\text{ester}\cdot\text{water} + H^+ \rightarrow \text{acid} + \text{alcohol} + H^+.$$

If the above-mentioned mechanism be correct, then the hydrolytic reaction should be very difficult to occur in the vapour phase, where the formation of the substrate-water complex will be greatly retarded and at the same time ions are not known to exist at least in the stable form. As there have been very few works on the reactions of organic compounds with water vapour, it occurred to the present authors that an inquiry into the nature of this type of reactions in the vapour phase would be interesting. Although Berthelot and Péan de St. Gilles[2] already noticed in their memorial work on the ester equilibrium that not only the formation but also the hydrolytic decomposition of ethyl acetate was greatly retarded in the vapour phase, and G. Harker[3] has recently pointed out that benzyl chloride is slowly attacked by liquid water but not by steam.

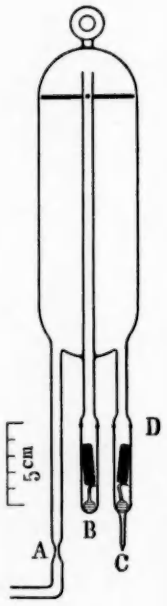

Fig. 1.
Reaction Vessel

The present paper is concerned with the non-reactivity of water vapour on benzyl chloride, the reaction of which with liquid water was already studied by one of the authors a few years ago,[4] and on ethyl acetate, which is one of the typical substances for the study of the hydrolytic reaction.

The reaction vessel shown in Fig. 1 is made of glass and has half a liter capacity. It was well cleaned with chromic mixture and steamed before every use. Weighed quantities of the ester and water were separately sealed in small thin-walled glass bottles of about 0.1 c.c. capacity. The ester-bottle was placed on the bottom of the center tube B and the water-bottle on the bottom of the tube C. A glass rod a few centimeters long was placed over each bottle, and both tubes B and C were connected by fusing at points D with respective side tubes in the lower part of the reaction vessel. The reaction vessel was then well pumped out through tube A and was sealed off at point A. After the small bottles containing substances were

(2) Berthelot and Péan de St. Gilles, *Ann. chim. phys.*, **65** (1865), 385; *Chem. Z.*, **7** (1862), 908.

(3) G. Harker, *J. Chem. Soc.*, **1924**, 500.

(4) T. Titani and K. Kurano, *Bull. Chem. Soc. Japan*, **6** (1931), 152.

broken by hammering them with the glass rods (caused by shaking), the reaction vessel was placed in an electrically heated air thermostat. The temperature was gradually raised up to the desired point, where it was able to be maintained constant automatically within ±1° for a long period. The quantities of the substances taken are shown in Table 1, where the total pressure exerted by the vaporized substances in the reaction vessel was calculated.

Table 1. Average amounts of the substances taken.

Substance	Temp. C.	Ester in mol	Water in mol	Total pressure calc. in atm.
Benzyl chloride	130°	0.0005	0.0004	0.06
	200°	0.001	0.005	0.30
Ethyl acetate	130°	0.001	0.001	0.13
	200°	0.002	0.008	0.78

After the reaction vessel was heated for a measured time, it was taken out of the thermostat and was quickly cooled down. As soon as it attained room temperature, a measured quantity of water (about 30 c.c. twice) was forced into the vessel through the right side tube C by breaking its capillary end in the water. The reaction vessel was rinsed in this way and whole water thus employed was carefully collected to be titrated against 0.02 N baryta, the titration being carried out as soon as possible. A few drops of the baryta were found enough, in most cases, to give an end point. A slight correction due to the carbonic acid from air had to be taken into consideration. The acidity thus determined was divided by the total mols of the ester employed, and then multiplied by 100. This value, which may be regarded as a percentage decomposition of the ester, is plotted against the duration of each run in hours (small circles in Fig. 2 and 3). Small triangles in these figures represent the results of the comparative experiments where the vapour of ester only was heated without an addition of water vapour. It will be seen from the figures that the degree of decomposition is very small in every case, on the whole 0.5% for benzyl chloride at 130°C. and 200°C. and 0.05% for ethyl acetate at 200°C. No trace of decomposition was found for ethyl acetate at 130°C. even after 150 hours' heating. This slight tendency to decompose is, moreover, always the same

irrespective of whether the esters are heated with or without an addition of water vapour. This slight decomposition is by no means caused by the hydrolytic reaction in vapour phase, but either by the hydrolysis in the

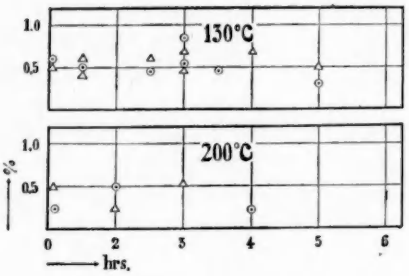

Fig. 2. Benzyl chloride

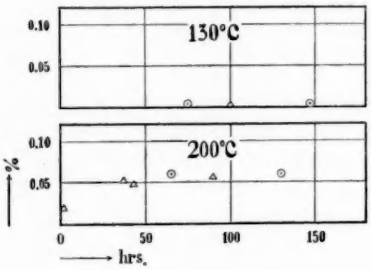

Fig. 3. Ethyl acetate

liquid phase during the washing and titration or by the thermal decomposition in the vapour phase. It was tried to avoid as far as possible the thermal decomposition at the temperatures employed by keeping the inner surface of the vessel clean and by gradually raising the temperature of the thermostat, so as not to superheat the esters in the liquid state. Nevertheless, the thermal effect became too remarkable at 300°C. to obtain a reproducible result above this temperature.

We may draw a following conclusion from the result so far obtained: (1) the hydrolysis is not a merely molecular reaction between ester and water molecules; (2) the heat of activation for the hydrolytic reaction in the vapour phase will be much larger than that of the thermal decomposition or polymerization.

Chemical Laboratory of the Osaka Imperial University
and
The Shiomi Institute for
Physical and Chemical Research.

HETEROGENEOUS CHEMICAL REACTIONS IN THE SILENT ELECTRIC DISCHARGE. XI.

By Susumu MIYAMOTO.

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The results of investigations obtained since the publication of the previous papers[1] are described in this paper. The apparatus and the procedure of the experiments are essentially the same as mentioned previously.

(1) **Potassium Thiocyanate.** Exp. 1. The quantity of potassium thiocyanate KSCN employed = 7.0 g. Time of silent electric discharge = 7 hours. On leaving the discharge tube the gas was passed first through distilled water and then through an alkaline solution.

The solid reaction product was dissolved in water, when a light yellow solution with the following properties was obtained. (1) It was alkaline. (2) The presence of sulphide was proved by means of sodium nitroprusside.[2] By analyzing the distilled water, through which the gaseous reaction product had been passed, the formation of hydrogen cyanide and hydrogen sulphide during the discharge was proved exactly as in the case of mercuric thiocyanate.[3]

Exp. 2. The quantity of hydrogen sulphide produced was determined. The quantity of potassium thiocyanate employed = 7.00 g. Time of silent electric discharge = 5 hours. Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 4.50 c.c.

From these experimental results it seems that the principal reactions in the discharge tube are expressed by the following equations, the reaction products being potassium hydroxide, potassium sulphide, hydrogen sulphide, and hydrogen cyanide.

$$2KSCN+H_2 = K_2S_2+2HCN,$$
$$K_2S_2+H_2 = K_2S+H_2S,$$
$$K_2S+2H_2O = 2KOH+H_2S.$$

(2) **Potassium Silver Cyanide.** Exp. 1. The quantity of potassium silver cyanide $KAg(CN)_2$ employed = 7.0 g. Time of silent electric

(1) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 724, 788, 914, 933; **54** (1933), 85, 202, 705, 1223; **55** (1934), 320.

(2) Treadwell, "Kurzes Lehrbuch der analytischen Chemie," 13th Ed., Vol. 1, p. 391.

(3) S. Miyamoto, this Bulletin, **9** (1934), 177.

discharge = 5 hours. Exactly as in the case of silver cyanide,[4] the formation of metallic silver and hydrogen cyanide was proved.

Exp. 2. The quantity of hydrogen cyanide produced was determined exactly as in the case of silver cyanide.[4] Potassium silver cyanide employed = 7.00 g. Time of silent electric discharge = 5 hours. The quantity of hydrogen cyanide produced = 0.0002 g.

From these experimental results it seems that the principal reaction in the discharge tube is expressed by

$$2KAg(CN)_2 + H_2 = 2KCN + 2Ag + 2HCN .$$

(3) **Calcium Thiocyanate.** Exp. 1. The quantity of calcium thiocyanate $Ca(SCN)_2 \cdot 3H_2O$ employed = 7.00 g. Time of silent electric discharge = 6 hours. A gas absorption bottle containing a potassium hydroxide solution was connected with the discharge tube.

The reaction product in the discharge tube was shaken with water; a yellow solution was obtained, which had the following properties. (1) It was acidic. (2) The absence of sulphide was proved by means of sodium nitroprusside. The evolution of hydrogen cyanide and hydrogen sulphide was proved by analyzing the alkaline solution, through which the gaseous reaction product had been passed on leaving the discharge tube.

Exp. 2. The quantity of hydrogen sulphide produced was determined. Calcium thiocyanate employed = 7.00 g. Time of silent electric discharge = 6 hours. Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 1.50 c.c.

From these experimental facts it seems that the principal reactions are expressed by the following equations:

$$Ca(SCN)_2 + 2H_2 = CaS + H_2S + 2HCN ,$$
$$CaS + 2H_2O = Ca(OH)_2 + H_2S .$$

(4) **Ammonium Thiocyanate.** Exp. 1. The quantity of ammonium thiocyanate NH_4SCN employed = 7.00 g. Time of silent electric discharge = 7 hours. On leaving the discharge tube the gas was passed first through an alkaline solution and then through dilute sulphuric acid.

On passing the electric current the powder in the discharge tube became slightly yellow. It was shaken with water and filtered. A small quantity of yellow powder remained, which is supposed to be sulphur. The filtrate was neutral and contained no appreciable quantity of sulphide. By analyzing the alkaline and sulphuric acid solutions through which the gas had been

(4) S. Miyamoto, this Bulletin, **9** (1934), 178.

passed, it was proved that hydrogen sulphide, hydrogen cyanide, and ammonia gas were reaction products.

Exp. 2. The quantity of hydrogen sulphide produced was determined. The quantity of ammonium thiocyanate employed = 7.00 g. Time of silent electric discharge = 6 hours. Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 2.00 c.c.

Exp. 3. The quantity of ammonia gas, absorbed by sulphuric acid, was determined in the usual manner.[5] The quantity of ammonium thiocyanate employed = 7.00 g. Time of silent electric discharge = 7 hours. Volume of sulphuric acid solution of 0.01000 normal, equivalent to the quantity of ammonia produced = 3.02 c.c.

From these experimental facts it seems that the principal reaction products are hydrogen sulphide, hydrogen cyanide, and ammonia gas, and that the reactions in the discharge tube are expressed by the following equations:

$$2NH_4SCN + H_2 = (NH_4)_2S_2 + 2HCN,$$
$$(NH_4)_2S_2 + H_2 = (NH_4)_2S + H_2S,$$
$$(NH_4)_2S = 2NH_3 + H_2S.$$

(5) **Sodium Thiosulphate.** Exp. 1. The quantity of sodium thiosulphate $Na_2S_2O_3 \cdot 5H_2O$ employed = 7.00 g. Time of silent electric discharge = 8 hours. A gas absorption bottle, containing a potassium hydroxide solution, was connected with the discharge tube. On passing the electric current no appreciable change was observed in the appearance of the powder in the discharge tube. Water was added to the solid reaction product, well shaken, and filtered. A small quantity of white powder, undoubtedly sulphur, remained. The filtrate had the following properties. (1) It was alkaline. (2) The absence of sulphide was proved by means of sodium nitroprusside. (3) The presence of sulphite was proved by the method of E. Votocek.[6] By analyzing the alkaline solution in the absorption bottle, it was proved that hydrogen sulphide was a reaction product.

It was thus proved that the principal reaction products are sulphite, sulphur, and hydrogen sulphide.

Exp. 2. The quantity of hydrogen sulphide produced was determined. The quantity of sodium thiosulphate employed = 7.00 g. Time of silent electric discharge = 6 hours. Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 3.82 c.c.

(5) Treadwell, "Kurzes Lehrbuch der analytischen Chemie.," 10th Ed., Vol. 2, p. 483.
(6) Treadwell-Hall, "Analytical Chemistry," 8th. Ed., Vol. 1, p. 416.

It seems that the principal reactions in the discharge tube are expressed by the following equations:

$$Na_2S_2O_3+H_2 = Na_2SO_3+H_2S,$$
$$4Na_2S_2O_3 = 3Na_2SO_4+Na_2S_5,$$
$$Na_2S_5 = Na_2S+4S,$$
$$S+H_2 = H_2S^{(7)},$$
$$Na_2SO_4+4H_2 = Na_2S+4H_2O^{(8)},$$
$$Na_2SO_3+3H_2 = Na_2S+3H_2O^{(9)}$$
$$Na_2S+2H_2O = 2NaOH+H_2S.$$

(6) **Magnesium Thiosulphate.** Exp. 1. The quantity of magnesium thiosulphate $MgS_2O_3 \cdot 6H_2O$ employed = 7.00 g. Time of silent electric discharge = 7 hours. Exactly as in the case of sodium thiosulphate it was proved that the principal reaction products are sulphite, sulphur, and hydrogen sulphide.

Exp. 2. The quantity of hydrogen sulphide produced was determined. The quantity of magnesium thiosulphate employed = 7.00 g. Time of silent electric discharge = 7 hours. Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 9.04 c.c.

From the results of the experiments it seems that the reactions in the discharge tube are expressed by the following equations:

$$MgS_2O_3+H_2 = MgSO_3+H_2S,$$
$$4MgS_2O_3 = 3MgSO_4+MgS+4S,$$
$$S+H_2 = H_2S,$$
$$MgSO_4+4H_2 = MgS+4H_2O^{(10)},$$
$$MgSO_3+3H_2 = MgS+3H_2O,$$
$$MgS+2H_2O = Mg(OH)_2+H_2S.$$

(7) **Barium Thiosulphate.** Exp. 1. The quantity of barium thiosulphate BaS_2O_3 employed = 7.00 g. Time of silent electric discharge = 6 hours. No appreciable change was observed in the appearance of the powder in the discharge tube. The solid reaction product was shaken with an excess of a sodium carbonate solution and filtered. The presence of sulphide and sulphite in the filtrate was proved exactly as in the case of sodium thiosulphate. It was proved that hydrogen sulphide was contained in the gas which left the discharge tube.

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(7) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 726.
(8) Ibid., **54** (1933), 86.
(9) Ibid., **54** (1933), 1231.
(10) Ibid., **53** (1932), 940.

Exp. 2. The quantity of hydrogen sulphide produced was determined. The quantity of barium thiosulphate employed = 7.00 g. Time of silent electric discharge = 6 hours. Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 1.50 c.c.

From these experimental results it seems that the reactions in the discharge tube are expressed by the following equations:

$$BaS_2O_3+H_2 = BaSO_3+H_2S,$$
$$4BaS_2O_3 = 3BaSO_4+BaS+4S,$$
$$BaSO_4+4H_2 = BaS+4H_2O^{(11)},$$
$$BaSO_3+3H_2 = BaS+3H_2O,$$
$$BaS+H_2 = Ba+H_2S^{(12)},$$
$$S+H_2 = H_2S.$$

(8) **Barium Chlorate.** Exp. 1. The quantity of barium chlorate $Ba(ClO_3)_2$ employed = 7.0 g. Time of silent electric discharge = 6 hours. The formation of chloride was proved in the usual manner.

Exp. 2. The quantity of chloride produced was determined exactly as in the case of potassium chlorate.[13] The quantity of barium chlorate employed = 7.00 g. Time of silent electric discharge = 6 hours. The volume of silver nitrate solution of 0.01000 normal, equivalent to the quantity of barium chloride produced = 15.10 c.c.

It was proved that the principal reaction in the discharge tube is expressed by

$$Ba(ClO_3)_2+6H_2 = BaCl_2+6H_2O.$$

Summary.

The chemical reactions under the silent electric discharge were studied when hydrogen reacted with the following inorganic solid substances.

(1) Potassium thiocyanate. Reaction products: hydrogen cyanide, hydrogen sulphide, and potassium sulphide.

(2) Potassium silver cyanide. Reaction products: silver and hydrogen cyanide.

(3) Calcium thiocyanate. Reaction products: hydrogen cyanide, hydrogen sulphide, and calcium hydroxide.

(11) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 935.
(12) Ibid., **53** (1932), 936.
(13) Ibid., **53** (1932), 731.

(4) Ammonium thiocyanate. Reaction products: hydrogen cyanide, ammonia, and hydrogen sulphide.

(5) Sodium thiosulphate. Reaction products: sodium sulphite, hydrogen sulphide, and sulphur.

(6) Magnesium thiosulphate. Reaction products: Magnesium sulphite, hydrogen sulphide, and sulphur.

(7) Barium thiosulphate. Reaction products: Barium sulphite, barium sulphide, hydrogen sulphide, and sulphur.

(8) Barium chlorate. Reaction products: barium chloride and water.

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Laboratory of Physical Chemistry,
Hiroshima University, Hiroshima.

THE COLLOIDAL BEHAVIOUR OF SERICIN. VII.*

By **Hideo KANEKO.**

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Sec. V. The Distribution of the Various Forms of Nitrogen in Sericin A and Sericin B.

The very close resemblance in properties between naturally occurring proteins and the higher synthetic polypeptides suggests that proteins are essentially formed by the condensation of varying numbers of groups of diamino- and monoamino-acids mainly by means of the peptide linkage.

R. Inoue, Abderhalden, and others have thoroughly investigated the nitrogen distribution in the true and the wild silks, and R. Inoue showed that fibroin and sericin are similar in the distribution of various forms of nitrogen, but their amino-acid compositions are greatly different. In order to compare the nitrogen distribution in sericin A and sericin B I have studied the same problem.

As for the structure of proteins, the molecule is found to consist essentially of a main-axis constructed with repeated three-atom-units in a zigzag chain. The middle carbon atom of the three-atom-unit joins an organic

* Continued from p. 474 of this volume, and concluded.

radical forming a long side-chain. If the side-chain be such a group as hydrogen, methyl, $CH_2(OH)-$, etc., that is, if the chain is formed of glycocoll, alanine, serine, etc., the molecule is permitted to pack together sufficiently closely to form fibers. In the case of silk fibroin, no less than 40 per cent. of the weight of the protein appears as glycocoll and a further 25 per cent. as alanine, so that most part of side-chain components in this protein is hydrogen-atom and methyl-group.

The contents of glycocoll and alanine in sericin are much less than in silk fibroin, so we can presume that in sericin molecules the main-axis components are smaller, but the side-chain components are greater than in fibroin. If a protein molecule has long, bulky side-chains, its main-axis cannot be brought into close approximation to that of another molecule of the same kind, but there will be a space left between them, and this space, in an aqueous solution, will obviously be filled up mainly with water and thus will be hydrated. The difference in the proportion of their components leads to easy separation into two proteins, fibroin and sericin, on boiling in water.

If the quantity of the nitrogen dissolved in water observed by R. Inoue and K. Kitazawa,[60] is compared with the lysine contents of silk, both are closely related as given in Table 105.

Table 105.

	N (%) dissolved in water by an hour boiling	Lysine content (%)
True silk	1.789	0.86
Antheraea Yamamai silk	1.339	0.19
Antheraea pernyi silk	0.428	0.03
Attacus cynthia silk	0.110	0.04

Amino-acid composition of sericin has been reported as shown in Table 106.

Table 106.

	Amino-acids	Turk[61]	Abderhalden	Inoue
Main-axis components	Glycocoll	—	1.1	4.38
	Alanine	—	10.10	8.86
	Serine	6.81	11.25	4.45

(60) R. Inoue and K. Kitazawa, *Bull. Seri. and Silk Ind. Japan*, **5** (1932), No. 1.
(61) Turk, *Z. physiol. Chem.*, **111** (1932), 69.

Table 106. (*Concluded*)

	Amino-acids	Turk	Abderhalden	Inoue
Side-chain components	Tyrosine	—	3.50	—
	Arginine	4.56	3.75	5.67
	Lysine	1.69	1.90	3.51
	Histidine	1.02	1.00	1.99

G. Yamanouchi[62] reported that in the silk gland of silkworms fibroin is surrounded by three sericin layers which are different in the degree of dying with acid fuchsin. The sericin in the outer layer, S_3, is dyed the most easily with this colour and the sericin in the middle layer, S_2, is difficult to be dyed.

I have shown that the cocoon layer having good "kaijo" possesses a greater capacity of adsorbing dyes than that having bad "kaijo", and that sericin A can adsorb many dyes like acid fuchsin, congo red, methylviolet, etc. stronger than sericin B. From these results it seems to me that these two components of sericin is separately secreted from different parts of the silk gland.

Six grams of sericin A or sericin B was dissolved in 120 c.c. of 30 per cent. hydrochloric acid and the solution was boiled in a tared flask under a reflex condenser until it gave no longer the biuret reaction. After 6 hours the hydrolysis of sericin was stopped and the solution was filtered, and diluted to 500 c.c. Various forms of nitrogen in sericin were determined by van Slyke's method. The results are given in Table 107.

Table 107.

	Sericin A (%)	Sericin B (%)	Sericin (%) (Inoue)	Fibroin (%) (Inoue)
Amide N	2.63	2.40	2.34	1.26
Humine N	2.51	2.47	1.93	2.05
Cystine N	0.70	0.83	0.70	0.40
Arginine N	8.43	5.14	5.67	4.85
Histidine N	0.69	2.48	0.49	6.74
Lysine N	4.34	4.83	4.88	0.13
Mono-amino N	76.74	80.53	81.52	75.19
Non-amino N	2.60	2.02	2.34	7.42
Hexon base N	14.16	13.28	11.74	12.12
Lys.+arg. N	12.77	9.97	10.55	4.98

(62) G. Yamanouchi, *J. Coll. Agri. Hokkaido Imp. Univ.*, **10** (1922), Part 4, 1–41.

As shown in Table 107, sericin A and sericin B are similar in the distribution of various forms of nitrogen. Sericin A is poorer in mono-amino nitrogen and richer in non-amino and hexon base nitrogen than sericin B. This difference may lead to different physico-chemical behaviours in viscosity, swelling, and gelatinization.

Block and Vickery[63] found that the basic amino components in keratins obtained from various sources have the following proportion :

$$\text{Histidine : Lysine : Arginine} = 1 : 4 : 12.$$

The results for sericin are shown in Table 108.

Table 108.

	Histidine : Lysine : Arginine
Sericin A	0.69 : 4.34 : 8.42 = 1 : 6.3 : 12.2
Sericin B	2.48 : 4.83 : 5.14 = 1 : 1.9 : 2.7
Fibroin	(Vickery and Block) 1 : 3.6 : 10.6

The molecular weights calculated on the assumption that the molecule of sericin contains one molecular equivalent of arginine, or lysine, are shown in Table 109.

Table 109.

	Sericin A	Sericin B
Arginine	17835	—
Lysine	20423	18718

The number obtained are to be regarded as the minimum values, and the molecular weight must be multiplied by a factor n, where n may be any integer.

Sec. VI. The Relation between Fibroin and Sericin.

Shelton and Johnson[64] showed that fibroin is probably a mixture of proteins loosely combined with one another. From the microscopical and chemical investigations we can presume that most of amino-acid components of silk fibroin consist of the main-axis components like glycocoll,

(63) Block and Vickery, *J. Biol. Chem.*, **93** (1931), 105, 113.
(64) Shelton and Johnson, *J. Ind. Eng.*, **22** (1930), 387.

alanine, etc. and a part of it consists of the side-chain components which are similar to those of sericin. The following orders hold good: fibroin > sericin A > sericin B, in main-axis components, fibroin < sericin B < sericin A, in side-chain components. The first order may be parallel with the easiness of precipitation with $(NH_4)_2SO_4$, and the second with their solubilities.

The solubility of sericin may depend for the most part on its basic components. And on boiling the sericin solution, the basic side-chain components may gradually separate off and the degree of hydration may be diminished. Therefore, the viscosity of the sericin solution may gradually diminish on boiling, and gelatinization may become imperfect. Then, the solubility of sericin in water may depend on the quantity of sericin, especially of sericin A, existing on the cocoon fibre and also on the quantity of the basic components.

Though the solubility of sericin increases on boiling under pressure, sericin B and a part of amorphous components of silk fibroin which are similar to those of sericin B may be dispersed into the solution. This may lead to decrease in the strength, elongation, and luster of silk fiber. For the same reason the ferment which decomposes the sericin B especially may also be able to attack on the amorphous components of fibroin, and the similar bad effects may be caused in the silk fiber.

Tyrosine contents of sericins and fibroin. Sericin was hydrolysed by six hours boiling with 25 per cent. sulphuric acid six times as much as the quantity of the sericin, the solution, after filtration, was diluted with twice its volume of water and neutralized with a strong solution of baryta, the excess of which was then quantitatively removed by dilute sulphuric acid. The solution, together with the water used for thoroughly washing the precipitate of barium sulphate, was then evaporated, until tyrosine crystallized out. It was collected; the filtrate was concentrated, and further crops of crystals were obtained until the mother liquor gave no longer Millon's reaction for tyrosine. It was purified by recrystallization from water, decolourization of the solution being effected by charcoal.

Table 110.

	Tyrosine	Gly./Tyr.
Sericin A	2.62%	2.38
Sericin B	5.53	0.84
Sericin (Abderhalden)	3.50	—
Fibroin (,,)	11.00	3.59

The tyrosine content of fibroin is on an average about 10 per cent., and it is a few times as great as that of sericin.

Sericin B contains much more tyrosine component than sericin A. The value of glycine : tyrosine is the greatest in fibroin, next in sericin A, and the least in sericin B. The above results lead to the conclusion that sericin is characteristically rich in side-chain components which have the great affinity with water, that fibroin is richer, on the contrary, in the main-axis components, and that in the distribution of nitrogen in the side-chain components sericin B is similar to the amorphous components of fibroin.

As is well known the high temperature and high relative humidity influence greatly the spinning velocity of liquid silk by silk worms. Y. Tanzawa[65] showed that the spinning velocity was proportional to the temperature under the same conditions. The greater the spinning velocity becomes, the more sericin B which is considered to exist closely near the fibroin layer is spinned out. Then the quantity of sericin B contained in the outer layer of cocoons increases with rising temperature, and this causes the retardation of the gelatinization of silk owing to the nature of sericin B, especially at high relative humidity. These unfavourable conditions may cause firm adherence of fibers and make them thinner.

PART III. CONCLUSION.

Sec. I. Varieties of Sericin.

The varieties of sericin which have been reported are summarized in Table 111.

Table 111.

Author	Varieties of sericin
K. Kodama	Sericin, Sericin pepton
K. Kondo	Sericin I, Sericin II.
Shelton and Johnson	Sericin A, Sericin B.
H. Kaneko	Sericin A, Sericin B.
T. Watanabe	Alcohol soluble and insoluble sericins.

K. Kondo prepared sericin for examination by soaking silk in water and treating it under 2.5–3 atmospheric pressures of steam for three hours. After three such treatments the water-soluble fraction was concentrated and the sericin was precipitated by adding two volumes of 80 per cent.

(65) Y. Tanzawa, *Sangyo Shimpō*, 1930, No. 448.

alcohol. This sericin was washed thoroughly with absolute alcohol and ether, and designated as sericin I. Sericin II was obtained by further concentrating the alcoholic filtrate and treating the concentrate with 80 per cent. alcohol. The resulting precipitate, washed with absolute alcohol and ether, gave a yellow powder.

Shelton and Johnson extracted sericin from silk with a small amount of water under a pressure of 50 cm. of mercury. They found that the whole protein was precipitated by means of alcohol and that after precipitation only a portion would again dissolve in cold water. They also found, as in the case of fibroin, that varying concentrations of $(NH_4)_2SO_4$ gave two kinds of precipitates, the first being a gelatinous substance insoluble in cold water.

T. Watanabe obtained two sericins from the sericin solution with alcohol. One was insoluble in 50 per cent. alcohol, and the other soluble in it. The results lead to the conclusion that sericin is not a simple compound, but it is a mixture of at least two different substances.

When I investigated the physico-chemical properties of the sericin solutions obtained from the cocoons having various "kaijo", I noticed many differences in their behaviours, though these differences may be partly due to the impurities contained in the cocoon layers. Then I obtained two different sericins from the sericin solution by the fractional precipitation with $(NH_4)_2SO_4$ as done by Shelton and Johnson. But I further found that the separation into these two components can be effected also by other electrolytes, by freezing, and by the electric current. The one which was easily salted out from solution by electrolytes was named "sericin A" and the other "sericin B." These two sericins were similar in the distribution of various forms of nitrogen, but very different in their physical properties.

Sec. II. The Distribution of Two Sericins on the Cocoon Fibers.

The distribution of sericin A and sericin B on the cocoon fibers has an intimate relation with the "kaijo" of cocoons, because they have different physico-chemical properties. The relation between the proportion of two sericins and "kaijo" are given in Table 112.

The better "kaijo" a cocoon has, the more sericin A is contained. H. H. Mosher[66] estimated two sericins in several raw silks by boiling cocoons in water at 115°C. under pressure.

In the same cocoon the outer layer is rich in sericin A and the inner layer in sericin B. So when we intend to reel cocoons at low temperature,

(66) H. H. Mosher, *American Dyestuff Reporter*, No. 11, 1932.

we must bear it in mind that the inner layer containing more sericin B should be thoroughly cooked.

Table 112.

"Kaijo"	Sericin A	Sericin B
Good	61.23%	38.76%
Middle	55.22	44.78
Bad	43.32	56.68

These two sericins seem to exist already in the liquid silk of the silkworm, and these may probably be secreted from different parts of the silk gland. Therefore, the "kaijo" of cocoons may primarily depend on the varieties of the cocoons and secondarily on the external conditions during the spinning of liquid silk and physical treatments.

The temperature influences the speed of spinning of liquid silk and may cause a change in the proportion of two sericins. The high relative humidity during the spinning retards the evaporation of water and consequently the gelatinization. Especially, heat may cause the transformation of sericin A into sericin B, so we must take care when we dry cocoons.

In gelatinization the inner and middle layers of cocoons are placed in worse conditions than the outer and further they may easily absorb the fatty matter from the pupa. These may lead to worse "kaijo."

Sec. III. The Micellar Structure of Sericins and Their Physico-Chemical Properties.

It has been considered that sericin is an amorphous substance. Although sericin and fibroin have remarkably different appearance, a micellar structure can be presumed for sericin, especially sericin A, as for the fibroin. The difference in the characteristic behaviours of these two proteins may be due to the difference in the proportion of the main-axis and side-chain components. Naturally fibroin is richer in the former component and sericin in the latter which has great affinity with water. As already described sericin A is coagulated in a fibrous form by many electrolytes, by freezing, and by applying the electric field in the sericin gel. The coagulate is considered to have a micellar structure.

The experiment concerning the distribution of various forms of nitrogen in sericin A and sericin B has shown that in the former more basic amino-acids are contained than in the latter. For this reason sericin A may be stronger hydrated in aqueous solution and in fact it shows higher viscosity, stronger swelling capacity, easier gelatinization, and heavier apparent specific gravity than sericin B.

Sericin A is apt to denature on drying, to turn slightly gray, and to shrink easily to a hard mass. Hence the solubility of sericin A in water is greatly reduced by drying though it seems that it ought to be more soluble than sericin B.

By the X-ray analysis of sericin powder it is shown that sericin has no micellar structure. But, it seems to me that this is the result of the shrinking property of sericin A as in the case of not stretched caouchouc. Recently K. Obara also has advanced the same opinion for the existence of a micellar structure in sericin on the ground of his microscopical investigation. Electrically charged sericin which tends to form molecular aggregates in solution, exists in solution as comparatively large particles associated with very large quantities of water. This aggregation of the sericin micellæ in aqueous solution varies with concentration and also with time. The physico-chemical properties of the sericin solution change, therefore, rapidly near the concentration of 0.3 per cent. as shown in Table 113. Effects of time of standing at the same concentration are given in Table 114.

Table 113.

	With increasing concentration, near 0.3%
Relative viscosity	rapidly increases
Surface tension	rapidly decreases
Diffusion coefficient	,, ,,
Specific rotation	,, ,,
Electric spec. conductivity	rapidly increases
Flocculation value	,, ,,
Gelatinization capacity	,, ,,
Depression of freezing point	,, ,,

Table 114.

	Maximum	Conc. (%)
Relative viscosity	about 90 min. later	0.32
Lowering of surface tension	,, 35 ,, ,,	0.40
Electric spec. conductivity	,, 30 ,, ,,	0.53
Gelatinization capacity	,, 120 ,, ,,	1.18
Protection against the decomposition of H_2O_2 by Pt sol	,, 90 ,, ,,	0.4–0.3

The aggregation of sericin micellæ depends also greatly on the temperature at the same concentration. From other experiments I can presume that the temperature of transformation of sol into gel corresponds to about 50°C.

Sec. IV. The Isoelectric Point of Sericin.

At the isoelectric point the dissolved protein is all electrically neutral. Such a solution is characterized by the tendency to aggregate and to take a high degree of turbidity and by the maximum ease in precipitation with alcohol or other lyophilic reagents. It has a greater surface activity. Dissolved protein always lowers the surface tension of water, but the effect is the greatest at the isoelectric point and is, therefore, due more to the electrically neutral protein than to the electrically charged. Hardy showed that the position of the maximum precipitation is influenced by the salt content. The isoelectric points obtained by various experiments are shown in Table 115 and 116.

Table 115. The isoelectric point of the natural sericin (mixed sericin).

	Good	Middle	Bad	Conc. (%)
Minimum relative viscosity	*p*H 3.95	4.12	4.18	0.2
Minimum surface tension of water	4.25	4.30	4.40	0.08
Minim. spec. rotation	4.24	4.30	—	0.2
Minim. emulsifying power	4.0	4.5	4.8	0.13
Maxim. precipitability with				
Methyl alcohol	4.0	—	—	0.2
Ethyl alcohol	3.8	—	—	,,
Acids	3.9	—	—	,,
$FeCl_3$, $AlCl_3$, etc.	4.2	—	—	,,
Nitrates	4.6	—	—	,,
Acetone	4.0	—	—	0.12
Minim. cataphoretic velocity	4.35	4.45	4.45	

Table 116. The isoelectric point of sericin A and sericin B.

	Sericin A	Sericin B
Minim. swelling	*p*H 3.80	4.50
Maxim. degree of turbidity	4.05	4.20
Minim. cataphoretic velocity	4.10	4.25
Minim. solubility	4.50	4.70

The isoelectric point of the natural sericin in which sericin A and B are mixed depends on the concentration and also on the " kaijo " of cocoons. In low concentrations the isoelectric point corresponds to about *p*H 4.0 in the sericin solution obtained from cocoons of good " kaijo ", and it is shifted to the alkaline side in the solution obtained from cocoons of bad " kaijo ".

The isoelectric points of sericin A and sericin B are respectively about *p*H 3.8 and *p*H 4.50. So we can understand that the isoelectric point of the sericin solution varies with the "kaijo" of cocoons, and that the sericin solution shows usually the isoelectric range in which sericin is capable of being precipitated by the addition of electrolytes or alcohol. If these two sericins are contained in equal amounts in the sericin solution, its isoelectric point may be probably *p*H 4.15.

Sec. V. The Molecular Weight of Sericin.

The probable molecular weight of sericin micellæ calculated from various data are given in Table 117. From these results the molecular weight of the sericin micellæ is considered to have an order of ten thousand.

Table 117. Molecular weight of sericin = 403 × n.

Calculated from	Mol. wt.	n
Viscosity	4026 (0.35%)	10
Diffusion coefficient	29441 (0.38%)	73
Depression of f. p.	8936 (0.34%)	22
Chemical analysis	19129 (sericin A)	47

Sec. VI. The Fibroin and Sericin, Two Proteins of Silk.

As shown by R. Inoue, fibroin and sericin are similar in the distribution of various forms of amino-acids, but very different in the proportion of the main-axis and the side-chain components. So the difference between fibroin and sericin exists in the proportion of components, their arrangement, and the manner in which they are linked.

The amorphous side-chain components of fibroin are especially similar to those of sericin B. The complete separation of sericin B from fibroin without doing damage to fibroin components may be theoretically difficult.

The formation of a film which protects the fibroin fiber must be necessary for the existence of sericin A which has probably a micellar structure.

In conclusion the author wishes to express his cordial thanks to Prof. Y. Shibata for his kind guidance and encouragement.

Uyeda College of Sericulture and Silk-Industry, Uyeda.